

# **Hydrogen as a Fuel in Maritime Applications**

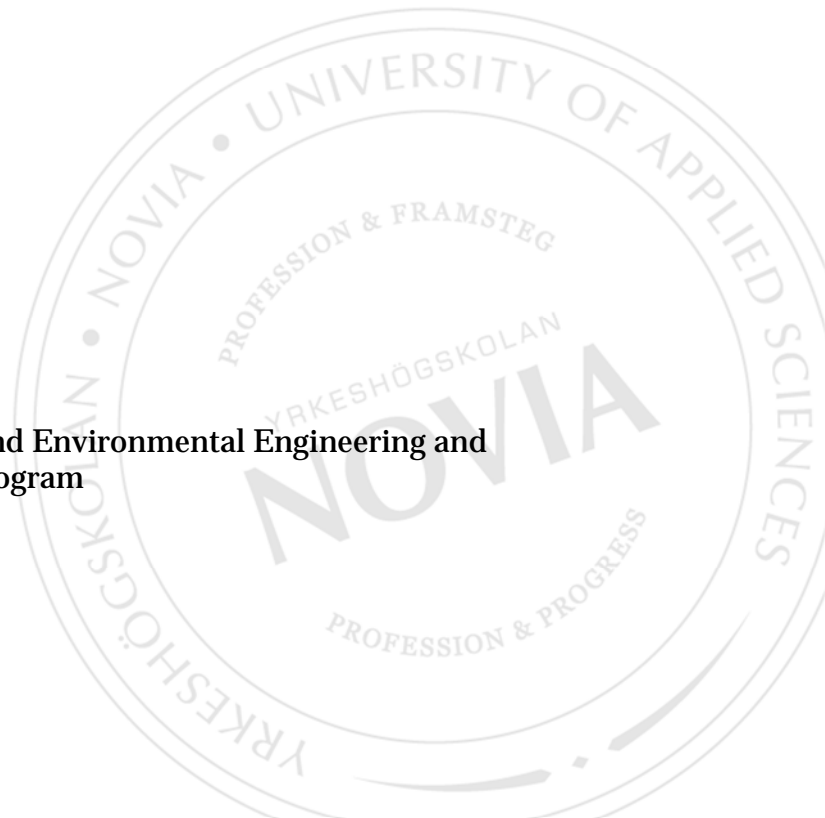
## **A Study on Implementing Hydrogen as a Fuel Source**

Pau Guitard Quer

Degree Thesis

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# BACHELOR'S THESIS

Author: Pau Guitard Quer

Degree Program: Double Degree in Energy and Environmental Engineering and Mechanical Engineering, Vaasa and Lleida

Supervisors: Charlotta Risku

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## Abstract

The thesis is divided in two main parts. The first part features an explanation of hydrogen, its characteristics and the different generation processes to produce it. The second part is the main part of the project. Firstly, the hydrogen gas Storage technology search section which contains a description of the technology and the different standards related on, and the study of the different alternatives of hydrogen gas tanks that can be suitable for the installation. Secondly, there is a refueling process section with an explanation of how the technology and the process of refueling works, and different fueling facilities around Europe and their further development. Following, the use of hydrogen as a cogeneration fuel to improve the A.C. system, with the different systems explanation and improvement process of using the hydrogen gas as a cooler gas. To conclude, the project ends up with a review of the different standards used on hydrogen gas storage.

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Language: English      Key words: hydrogen, fuel cell, storage, maritime, boat, heat exchange

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## Terminology and abbreviations

A.C. system	Air Conditioning System
°C	Degree Celsius
K	Degree Kelvin
W	Watt
kW	Kilowatt ( $10^3$ W)
kW/h	Kilowatt hour
BTU	British Thermal Unit
V	Volt
A	Ampere
g	Grams
kg	Kilogram
kg/s	Kilogram per second
cm <sup>3</sup>	Cubic centimeters
l	Liters
l.p.m.	Liters per minute
m	Meter
MPa	Megapascal
Nm <sup>3</sup>	Normal cubic meter
J	Joule
MJ	Megajoule ( $10^6$ J)
kJ	Kilojoule ( $10^3$ J)
mJ	Millijoule ( $10^{-3}$ J)
s	second
CH <sub>4</sub>	Methane
H <sub>2</sub> O	Water
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
O <sub>2</sub>	Oxygen
TiO <sub>2</sub>	Titanium Dioxide
$\Delta H^0$	Enthalpy increase
e <sup>-</sup>	Electron
CNG	Compressed Natural Gas
CHG	Compressed Hydrogen Gas
ICE	Internal Combustion Chamber
PRD	Pressure Release Device

# 1 Introduction

## 1.1 Background

Among naval history there have been different ways of powering ships. All the different evolutions of the powering systems have changed at the same time as the humanity has evolved, as an improvement in the different industrial revolutions. The development of a new energy has been included in all the different types of vehicles existing in that particular century or helped developing a new one.

The first transport use, apart from the human power, has been the use of animal power as a carrying transport. The usage of animal power as a way of transport has been used since the domestication of animals. After that historical achievement humanity has added extra machinery to the animals for carrying more and more weight. However the first and only transportation vehicle in the human history that have never used animal power as the main power source is the maritime transport. The main power source in this case has been the use of sails at the top of boats or ships, in that case depending on the region of the world, the sails have had different structures to sail under different weather conditions and seas, as we can see the difference between the Egyptian boats and the Polynesian boats, to the most similar structures that were developed at the end of middle ages.

All those pre-industrial revolution boats had the same main energy source, using the wind or human power as the main “fuel”. During the industrial revolution era and after, three different stages of development can be seen depending on their main energy source [14].

The first era started after the invention of the steam engine using carbon as the main energy source and last all over the industrial revolution until the development of the internal combustion engine. It is considered that takes the whole XIX century. The second era started in the XX century and nowadays it is still being developed. The main aspect of the second era is the use of petrol as an energy supply during the whole era and since the late 50's the use of nuclear energy.

Nowadays we are in the third and newest era, the era of the alternative energy supplies. Those alternative energy supplies can be different types but they all have the same characteristic, all are renewable sources to reduce the amount of pollutant emission emitted

during the first two eras and to achieve a sustainable future for the maritime sector. This third era is taking place at the same time as the second era.

In this thesis it will develop a study to achieve the porpoise of the third era, use an alternative source to reduce the dependence on non-renewable sources.

## **1.2 Objective**

The objective of this thesis is to study the feasibility of using the hydrogen and fuel cell technology in a boat and use it to generate electricity during night time and have reduce the noise and vibrations. During the development of this thesis, another possible use of the hydrogen has been found. This new use is as a source of producing cold to use it for cold water production for the A.C system.

The main aim is to achieve an approximation of energy output at electricity and cold production.

## **1.3 Method**

The method used in this thesis is divided into two main parts.

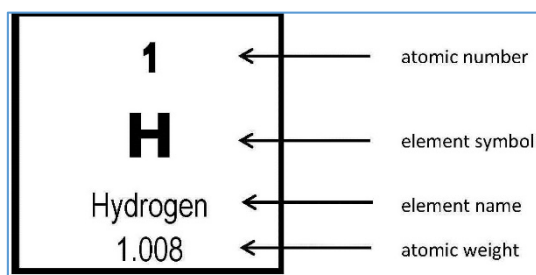
The first part is a theoretical part related to the hydrogen, explaining characteristics of hydrogen and the different technologies to be produced. To do this part has been done a search at the different available technical literature.

The second part is the main study of the technology. Before analyzing and studying their feasibility in the system there is a theoretical part. For that study some companies have been contacted to ask for their technology and expertise in the field. Also it has been used the different technology data and information given by Baltic Yachts.

## 2 Hydrogen

### 2.1 Characteristics

Hydrogen is the lightest and abundant chemical element in the universe. It is the first element in the periodic table, with the H symbol, and the atom it is formed by one proton and one electron. At ambient temperature and at atmospheric pressure, hydrogen is a colorless, odorless and tasteless, normally found in a diatomic form ( $H_2$ ), and its stable state is as a gas. Hydrogen it can be found on Earth in large quantities as water, and also it can be found as a gas in tiny amounts in the atmosphere. In not a natural way, hydrogen can be found when natural gas is heated. At the following table (table 1) and figure (figure 1) it can be seen the different physical and chemical characteristics of hydrogen [7].



1	← atomic number
H	← element symbol
Hydrogen	← element name
1.008	← atomic weight

Figure 1: Hydrogen at the periodic table.

Table 1: Hydrogen characteristics

HYDROGEN CHARACTERISTICS			
Atomic number	1	Density [g/cm <sup>3</sup> ] (liquid)	0.0708
Element Symbol	H	Density [g/l] (liquid)	0.0899
Atomic mass	1.00794	Melting point [°C]	-259.16
Electron configuration	1s <sup>1</sup>	Boiling point [°C]	-252.879
Electronegativity	2.20	Thermal conductivity [W/m*K]	0.1805

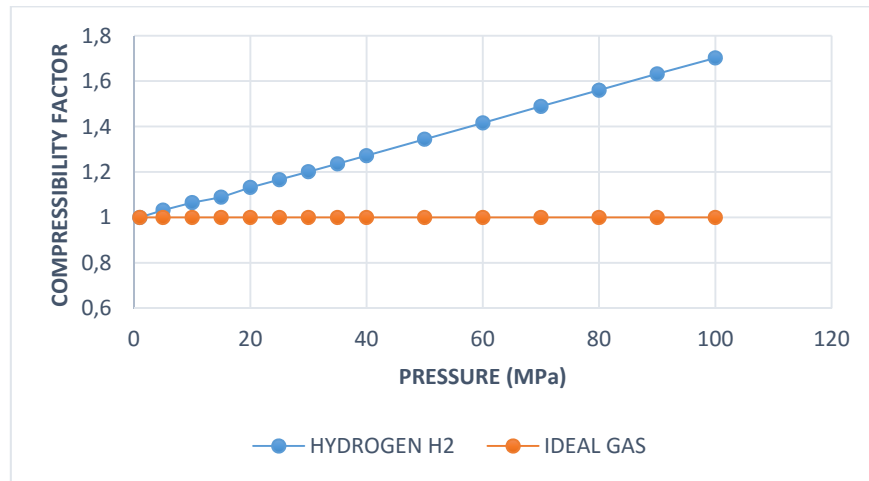
### 2.2 Compressibility

For having a good technological application, the volume of hydrogen is a very important characteristic, regarding storage. Due to hydrogen it is presented in nature as a gas, because has melting point at a really low temperature, -252.88 °C, has a dependence on pressure and temperature. As a result of the high compressibility characteristic of the hydrogen gas, it is needed a table of compressibility factor. The following table (table 2) and graphic (graphic

1) shows the compressibility factor ( $Z$ ) of hydrogen at different pressures and 0 °C (273.15 K) [6]:

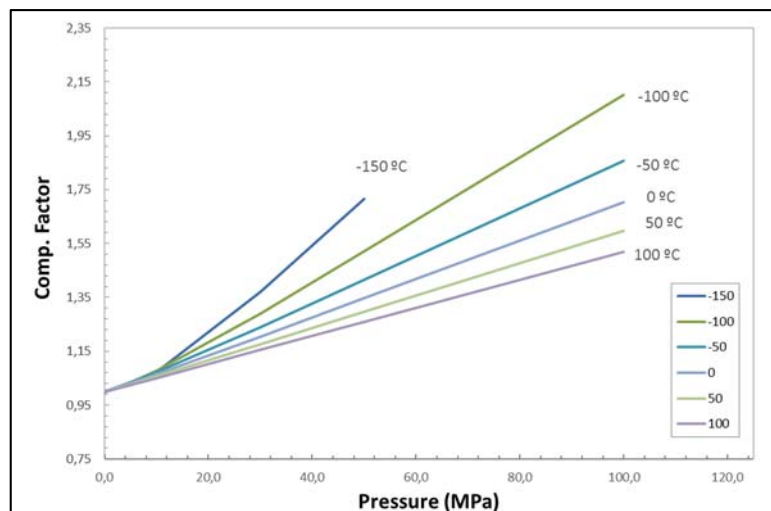
Table 2: Compressibility factor ( $Z$ ) of hydrogen

PRESSURE (MPa)	1	5	10	15	20	25	30	35	40	50	60	70	80	90	100
COMP. FACTOR	1	1.032	1.065	1.089	1.132	1.166	1.201	1.236	1.272	1.344	1.416	1.489	1.56	1.632	1.702



Graphic 1: Hydrogen and ideal gas compressibility factor ( $Z$ )

The compressibility factor also depends on the temperature. As it can be seen on the following graphic (graphic 2) [26], with a low temperature the compressibility factor increases rapidly, but it allows a lower maximum pressure.



Graphic 2: Compressor factor depending on the pressure and temperature

In the following part it will be explained how the compressibility factor table works. The compressibility factor ( $Z$ ) is an empirical or experimental predicted value that measure the deviation of the real molar volume occupied by a gas and the molar volume that would occupy if it was an ideal gas, as it can be seen in the following equation [24]:

$$(2.1) Z = \frac{V_{real}}{V_{ideal}}$$

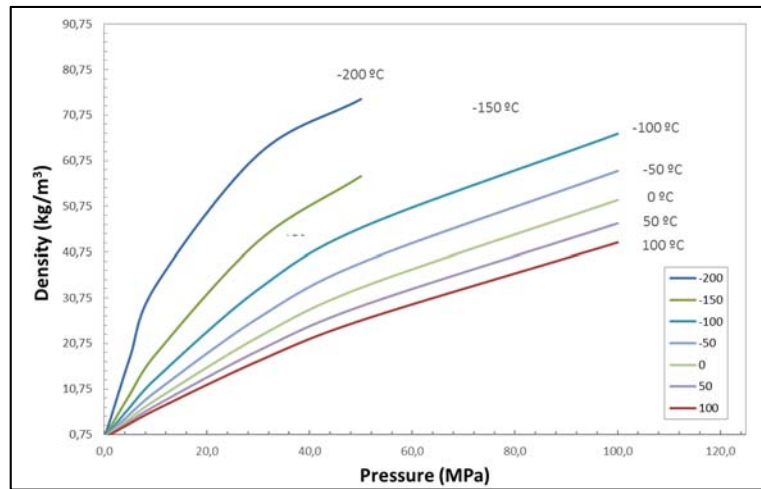
From the compressibility factor equation (2.1) and using the equation of the ideal gases (2.2) it can be obtained the another equation (2.3), which sets the relationship between the compressibility factor, the real volume and the pressure depending on the temperature.

$$(2.2) P \cdot V_{ideal} = n \cdot R \cdot T \quad \left[ (2.1) Z = \frac{V_{real}}{V_{ideal}} \rightarrow V_{ideal} = \frac{V_{real}}{Z} \right] \rightarrow (2.3) \frac{P \cdot V_{real}}{Z} = n \cdot R \cdot T$$

Where:

- P = Absolute pressure [atm]
- V = Volume [l]
- R = Ideal Gas constant =  $0.082057 \left[ \frac{atm \cdot l}{mol \cdot K} \right]$
- T = Temperature [K]
- Z = Compressibility factor
- n = number of moles [mol]

As it can be seen in the following graphic (graphic 1), changes on the temperature and pressure of the gas have big affections on the density of the hydrogen gas. That characteristic is the main aim to be developed at the hydrogen gas tank storage [26].



Graphic 3: Density depending on the pressure and temperature

At graphic 2 and graphic 3, the data used for realizing the graphical representation has been taken from the U.S. Department of Energy hydrogen data book [26]. That database of hydrogen is part of the Hydrogen Analysis Resource Center, where apart from databases there are some resources related to hydrogen ready for being downloaded.

## 2.3 Energy carrier

Hydrogen has been used as an energy equivalence due to their wide range of different uses it can be taken part, and that is a characteristic to be aware of. The energetic characteristics of the hydrogen can be seen at the following table (table 3) [23].

Table 3: Energetic characteristics of the hydrogen

WEIGHT (kg)	GAS (Nm <sup>3</sup> )	LIQUID (l)	ENERGY (MJ)
1	11.12	14.12	120
0.0899	1	1.27	10.8
0.0708	0.788	1	8.495
0.00833	0.0926	0.1177	1

The hydrogen as an energy source has different uses depending on the needs of the industrial application it is being used, it can be used as a liquid or as a gas. It would be better to compare the energetic characteristic of different fuels and gases with the characteristics of the hydrogen. Those characteristics are in the following table [22]:

Table 4: Energetic characteristics comparison.

PROPERTY	HYDROGEN	METHANOL	METHANE	PROPANE	GASOLINE
Minimum energy for ignition (mJ)	0.02	-	0.29	0.25	0.24
Flame temperature (°C)	2,045		1,875		2,200
Auto-ignition temperature in air (°C)	585	385	540	510	230-500
Maximum flame velocity (m·s <sup>-1</sup> )	3.46	-	0.43	0.47	
Range of flammability in air (vol. %)	4-75	7-36	5-15	2.5-9.3	1.0-7.6
Range of explosivity in air (vol. %)	13-65		6.3-13.5		1.1-3.3
Diffusion coefficient in air (10 <sup>-4</sup> m <sup>2</sup> ·s <sup>-1</sup> )	0.61	0.16	0.20	0.10	0.05

Hydrogen has been used as a fuel by placing it inside the combustion chamber, as a gas or as a liquid. It have two different ways to use hydrogen inside the combustion chamber, as a part of the gasoline mixture or as the only fuel.

The use of hydrogen as the only fuel has been tried to get for a long time. Their use have some advantages and disadvantages [9].

- Wide flammability range in comparison with all other fuels. That characteristic indicates that hydrogen can be burned over a wide range of fuel-air mixtures.
- Low ignition energy point. It means that is needed less energy to ignite the hydrogen fuel, it is more suitable to use it. On the other hand, there can be some problems related to the possible premature ignitions, flashbacks and with the wide flammability range, which can be ignited by a hot spot.

- Small quenching distance. This characteristic makes the flames move closer to the internal combustion chamber wall before being extinguished and can cause a flame from the hydrogen-air mixture to pass through a valve during the closing process.
- High autoignition temperature. That characteristic has important implication with the compression process, what will affect the compression ratio that the engine can use because of the increase of the temperature during the process. It has to take in consideration trying to avoid a compression rate where the ignition temperature is reached.

$$(2.4) T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

Where:

$V_1/V_2$	= compression ratio
$T_1$	= initial temperature (K)
$T_2$	= final temperature (K)
$\gamma$	= specific heats ratio

- High flame speed. Hydrogen has high flame speed at stoichiometric ratios. This characteristic means that these engines can come closer to the thermodynamic ideal engine cycle.
- High diffusivity. This characteristic it is considered a great advantage because it means that inside the internal combustion chamber is produced a uniform mixture of fuel and air.
- Low density. There are two main problems related to the low density of the hydrogen. The first one is the storage volume necessary to give a vehicle an adequate range of usage. The second it is the low density of the hydrogen-air mixture, what affects decreasing the output power.

Depending on the fuel method used to power the internal combustion chamber, the output power compared to the gasoline can vary from 85% (intake manifold injection) to 120% (high pressure injection). In the following figure (figure 5) there is a comparison of the combustion chambers volumes and energy content for the gasoline and different types of hydrogen fueled engines [12].

Table 5: Comparison between gasoline and hydrogen fueled engines.

	<b>LIQUID GASOLINE</b>	<b>GASEOUS HYDROGEN PRE-MIXED</b>	<b>LIQUID HYDROGEN PRE-MIXED</b>	<b>HIGH PRESSURE GASEOUS HYDROGEN INJECTION</b>
Volume (cm <sup>3</sup> )	1,000	1,000	1,370	1,420
Fuel (cm <sup>3</sup> )	17	300	405	420
Air (cm <sup>3</sup> )	983	700	965	1,000
Energy (kJ)	3.5	3	4	4.2
%	100	85	115	120

The second type is using a mixture of hydrogen and a hydrocarbon fuel. The use of this fuel mixture intends to improve the fuel economy and/or the power output by changing the fuel ratio, the ignition timing and various control systems such as emissions and the electronic equipment. This type of fueled engines can produce some advantages and disadvantages such as:

- Reduction of carbon monoxide emissions up to 90% because hydrogen acts as a catalyst to promote combustion.
- Reduction of particles emissions, especially organic particles up to 70%.
- Reduction of exhaust gas temperatures up to 65 °C.
- Increase of engine power, horsepower, up to 12%.
- This type of fuel does not reduces the NO<sub>x</sub> emissions, and in some cases increase them.

### 3 Hydrogen production

Hydrogen is not a primary energy source and needs to be obtained using different processes that requires different energy consumptions. As it is a manufactured product, the final energetic balance and the environmental impact are involved in their process. Nowadays, up to 96% of hydrogen production is generated using conventional energy sources with a high pollutant gases emissions.

The main aim with the hydrogen production is to extract and isolate the independent molecules of hydrogen at the purity level required for the application. The processes of hydrogen production can be divided into three main groups depending on the raw material used and the process for obtaining hydrogen. The main processes for obtaining the hydrogen are the following ones and also are divided into the three main groups. The following sections describe and explain the basic parts of different processes:

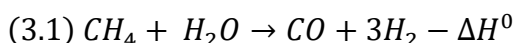
- Fossil Fuel based
  - o Steam reforming of natural gas.
  - o Partial oxidation, autothermal and dry reforming.
- Hybrid Solar-Fossil based
  - o Direct thermal or catalytic splitting of water.
- 100% Renewable based
  - o Water electrolysis.
  - o Gasification and woody biomass conversion.
  - o Biological hydrogen production.
  - o Photodissociation.

The different hydrogen production processes in this chapter have been taken from the book, *Hydrogen and Fuel Cells: Emerging technologies and applications* from Bent Sørensen [22], as a source for their explanation.

### 3.1 Fossil fuel based

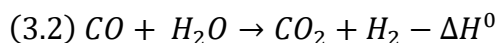
#### 3.1.1 Steam reforming of natural gas

[22] Nowadays the industrial way of producing hydrogen is using methane,  $\text{CH}_4$ , which is the main part of the natural gas. It is used a mixture of methane and water vapor at an elevated temperature that reacts at a strongly endothermic reaction,



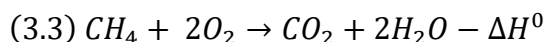
The carbon monoxide and hydrogen placed at the right side of the (3.1) reaction it is called “synthesis gas” and requires a catalyst, nickel or more complex mixtures of nickel with aluminum oxide, cobalt, alkali, and rare-earth, at a high temperature of about 850 °C and a pressure of 2.5 MPa. During the reaction (3.1) the increase of enthalpy is positive.

The whole process is controlled due to the reacting temperature and pressure, as mentioned, and the design of a reactor used for the reforming process. There are other reactions that could take place in the reformer, such as the inverse of the reaction (3.1). In order to obtain a high efficiency during the conversion, some heat inputs are taken from cooling the reactants and from the heat outputs that took place at the water-gas “shift-reaction” that usually takes place in a separate reactor,

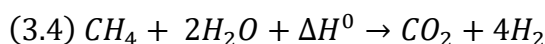


During this reaction (3.2) the increase of enthalpy is negative, and the heat is recovered and recycled back to the first reaction (3.1). That requires two heat exchangers and that is the main reason of the high cost of producing hydrogen using the steam reformer process.

Although, industrial steam reformers usually use direct combustion of a part of the primary methane to provide the heat required at the reaction (3.1),



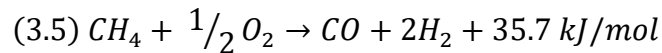
the reaction will remain at a gaseous state due to their temperature and pressure. The heat evolution with products in gas form is called “lower heat value” of methane, while the one including the heat of the condensation to liquid form is called “upper heat value”. Combining the reactions (3.1) and (3.2) produce



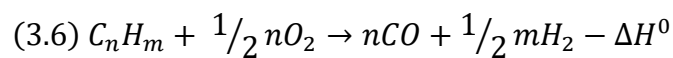
As a chemical energy conversion process, the reaction (3.4) has the ideal efficiency of 100% because the sum of the burning value for  $\text{CH}_4$  and the required heat input to the process equals the burning value of  $4\text{H}_2$ .

### 3.1.2 Partial oxidation, autothermal and dry reforming

[22] The moderately exothermic catalytic partial oxidation process for methane,

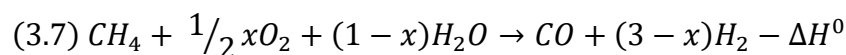


or more generally,



is considerably more rapid than steam reforming. When oxygen and methane are passed over a suitable catalyst, the reaction (3.5) occurs. When oxygen is supplied though air, nitrogen has to be removed from the hydrogen. This usually takes place at a separate stage following the oxidation reactor. Partial oxidation is a good choice for small scale conversion needs, such as in a motor vehicle with fuel cells because the process can be stopped and started as required.

When in progress it provides elevated temperatures that could start steam reforming at the same time as the oxidation process. This is called “autothermal” reforming and involves all the reactions mentioned plus a stoichiometric variations on (3.5) in the possible presence of water,



while  $x < 1$ , depending on the presence of water.

Hydrogen production by partial oxidation from methane increases while increasing the process temperature, but reaches its maximum at 1,000 K. The theoretical efficiency is the same as in the steam reforming, but with a less consume of water.

## **3.2 Hybrid solar-fossil based**

### **3.2.1 Direct thermal or catalytic splitting of water**

[22] This process of producing hydrogen is from thermal decomposition of water, as in the direct process it is required temperatures higher than 3,000 K, which with the actual technology it is not a viable solution, there have been some studies to achieve the decomposition below 800 °C using cyclic chemical processes and catalysts. These thermochemical or water-splitting cycles were originally designed to reduce the required temperature in nuclear reactors.

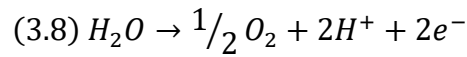
## **3.3 100% Renewable based**

### **3.3.1 Water electrolysis**

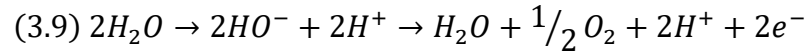
[22] Consists on decomposition using the electricity that splits water into hydrogen and oxygen. It is an industrial process known for a long time, demonstrated by Faraday on 1820 and widely used since 1890, which allows having a high level of development and products on the market with a high level of efficiency. Those machinery processes are modular, what allows a high adaptability characteristic due to their production, either being big or small hydrogen production quantities.

The electrolysis process produces a high purity hydrogen that it is relatively easy to complement renewable energy sources that could help the reduction of fossil fuels dependency and improve the use of them. As it just mentioned, the cost of hydrogen production using water electrolysis depends mainly due to the cost of electricity. In places and moments with overproduction of electricity it makes hydrogen storage a suitable way to energy storage for later uses.

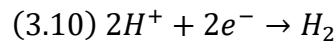
Conventional electrolysis uses an aqueous alkaline electrolyte with the positive and negative electrode areas separated by a microporous diaphragm. The reaction that takes place at the positive electrode is,



Where electrons are leaving the cell using an external circuit and where the three products may be formed by a two-step process,



The reaction at the negative electrode is



taking the electrons from the external circuit produced at the positive electrode, as it can be seen on the following figure (figure 2).

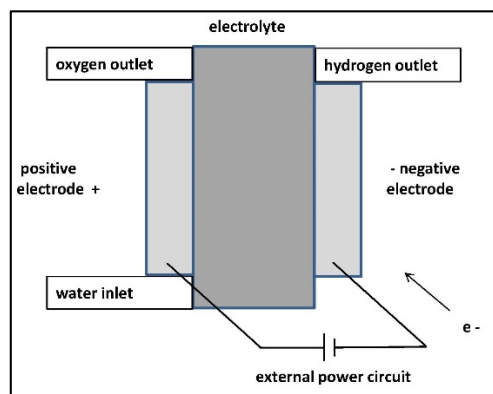


Figure 2: Water electrolysis cell schematic.

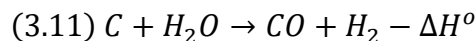
The hydrogen ions are transported through the electrolyte by the electrical potential difference. The role of the alkaline component is to improve on the poor ion conductivity of water. However, to avoid a strong increase in alkaline corrosion off the electrodes, the temperature of the reaction must have values below 100 °C. Although, if the ambient temperature is used, 25 °C, it would produce a really slow process.

### 3.3.2 Gasification and woody biomass conversion

[22] An emerging technology for producing hydrogen from natural gas or heavy fuel oil, although with substantial electricity inputs, is high-temperature plasma-arc gasification, based on which has been developed a pilot plant, which operates on natural gas at 1,600 °C, at Kvaerner Engineering in Norway. The resulting products are in energy terms:

- 48% Hydrogen.
- 40% Carbon.
- 10% Steam.

Gasification is seen as a key pathway towards when starting from coal or lignin-containing biomass. The gasification takes place by heating with steam:



For biomass, the carbon is at the beginning contained in a range of sugar-like compounds, such as cellulose materials. Without catalyst, the gasification takes place at temperatures higher than 900 °C, but using a suitable catalyst the temperatures can drop around 700 °C. If it is needed to produce additional hydrogen by the shift reaction (3.2), it has to take place in a separate reactor operating at a temperature of about 425 °C.

Coal may be gasified in situ, before extraction. If it has been already mined, there are different methods to do the gasification such the Lurgi fixed-bed gasifier and the Koppers-Totzek gasifier. Peat and wood can be gasified in a similar way as coal.

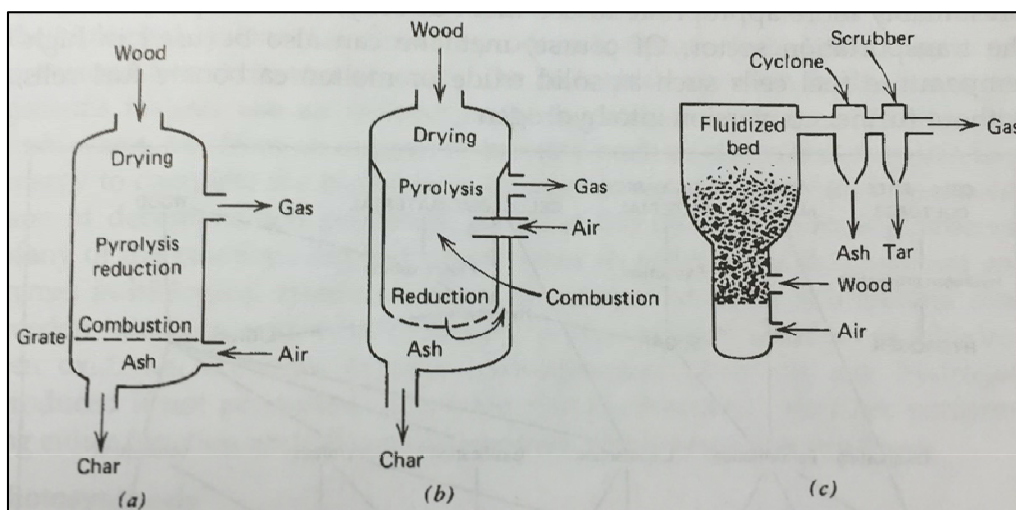


Figure 3: Gasifier types. (From B. Sørensen, *Hydrogen and fuel cells; Emerging technologies and applications*).

As it can be seen in the previous image (Figure 4) there are three types of gasifiers. The updraft gasifier (Figure 4.a) is much direct and easy to produce, but it has a drawback that it is the high amount of oil, tar and corrosive chemical formatted in the pyrolysis zone. This problem is solved in the downdraft gasifier (Figure 4.b), where all those products produced in the pyrolysis zone pass through a hot charcoal bed in the lowest part of the gasifier and become cracked to gases or char. The fluidised bed reactor (Figure 4.c) can be better for large-scale operations because the passage time is smaller, but there is a drawback, and it is that the ashes and tars are carried with the gas and it has to be removed by using cyclones and scrubbers.

The gas produced by gasification of biomass it can be considered a “medium-quality gas” and it may be used directly to internal combustion engines or drive heat pump compressors.

### **3.3.3 Biological hydrogen production**

[22] The production of hydrogen using biomass can be achieved by means of biological fermentation or using another bacteria or algae decomposition of water or another suitable substance. The conversion process has to be taken place or in the dark or with the assistance of light. During the growth of the biological substance will be required an energy input, normally from sunlight, and because there are several conversion processes, there are several efficiencies involved: from primary energy source to the biological material, from the energy in the biological material to the energy in the hydrogen production, or the efficiency from the solar radiation to the hydrogen. Because the production of hydrogen it is not a natural process there are some modifications that have to be done to achieve this purpose. Plants have a very low efficiency rate of converting solar energy, which increase the cost of equipment required to be used.

Some primary sources, or substrates, for biological hydrogen production require the addition of water in case of direct photolysis process and as the primary substrate for photosystem. In this cases the biological system could directly produce the hydrogen.

On the other hand, there are some organisms that use an indirect path to produce the hydrogen, instead of using water as a substrate using other organic compounds that require less energy to complete the conversion. In organic waste fermentation the hydrogen is produced from a succession of decomposition processes. Many of the reactions depends on enzymes to produce the hydrogen.

### **3.3.4 Photodisociation**

[22] Photovoltaic and photoelectrochemical devices can be modified to deliver hydrogen directly rather than electricity. The main problem using this technology is that the production of hydrogen does not start until enough cell voltage is reached, and also the problem of separating the hydrogen from the oxygen for reasons of safety.

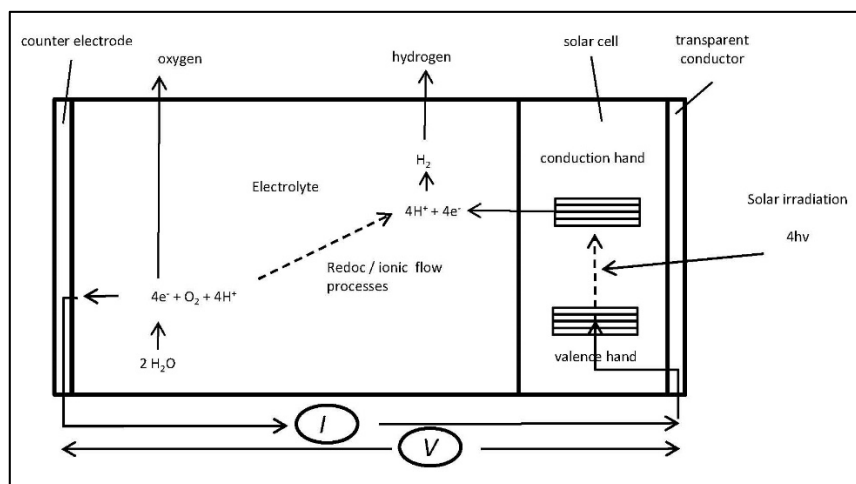


Figure 4: Solar hydrogen producing cell schematics.

As it can be seen in the previous image (figure 5), one of the terminal electrodes is separated from the solar cell to make space for an electrolyte containing water and some ion-conducting medium. This design is known from photoelectrochemical solar power cells, where the photoelectrode is usually made of nanocrystalline  $\text{TiO}_2$  and covered by a metal acting as a photo-sensitiser. The voltage across the electrolyte is not a constant quantity, depends on the chemical reactions taking place in the electrolyte.

### 3.4 Hydrogen production summary

The industrial way of hydrogen production since the previous century until nowadays is Steam Reforming. As a reference, in 2010 more than the 95% of the hydrogen produced in the United States of America was produced using this technology. This method is used because, apart is a technology known for decades, it is the cheapest process to produce hydrogen, as it can be seen in the following table (table 6)[19].

Table 6: Hydrogen production costs.

METHOD	CRITICAL PARAMETERS / ASSUMPTIONS	COSTS (\$/kWh)
<b>FUEL FOSSIL BASED</b>		
Steam Reforming of NG	Sensitive to feedstock process	0.02-0.04
Coal Gasification	High capital investment	0.05-0.07
POX Crude Oil	High capital investment	0.03-0.05
<b>HYBRID SOLAR-FOSSIL BASED</b>		
Solar Reforming of NG	Solar process heat: 0.016 \$/kWh	Syngas: 0.03
Solar Decomposition of NG	Credit for C (gr) sale	0.03-0.05
Solar SynMet	Sensitive to $\eta$ and heat recovery	0.10-0.14
Solar Splitting of $\text{H}_2\text{S}$	Credit for $\text{S}_2$ sale	0.04-0.05

100% RENEWABLE BASED		
Solar Splitting of H <sub>2</sub> O	Materials: H <sub>2</sub> O/O <sub>2</sub> separation	
Trough System + Electrolysis	Electricity @ 0.12 \$/kWh	0.20
Power Tower System + Electrolysis	Electricity @ 0.08 \$/kWh	0.16
Dish Stirling System + Electrolysis	Electricity @ 0.18 \$/kWh	0.26
Solar High-Temperature Electrolysis	Power Tower System: T sensitive	0.13
PV Electricity + Electrolysis	Projection for 2,010	0.20-0.30
Solar Photo-electrochemical		
Solar ZnO/Zn Cycle	High Temperature, materials	0.13-0.15
Wind Electricity + Electrolysis	Electricity @ 0.06 \$/kWh	0.10-0.17
Biomass Gasification		0.06-0.10
Hydro Electricity + Electrolysis		0.10

As it can be seen, the 100% renewable based hydrogen production are the most expensive processes to produce hydrogen, while the fossil-fuel based processes are the cheapest, although here are some 100% renewable based processes that have no production costs, rather than the installation costs. From the previous table (table 6) can be concluded that there is a need for more research about the renewable based processes to achieve the same level of costs as the cheapest processes.

## 4 Hydrogen storage

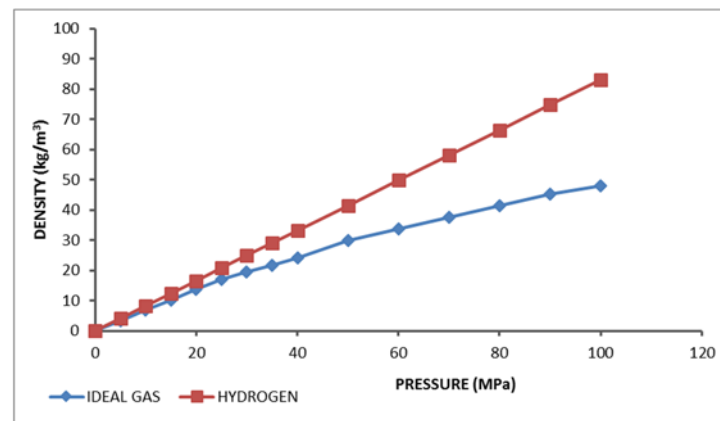
There are different ways to store the hydrogen and depending on the application it is more suitable to use one or another. In transport sector applications, the storage tank has to be placed within the vehicle, meaning, the volume and the weight cannot have to overpass the specifications and performance of the vehicle. The same happens with the building-integrated applications, where the storage volume usually is restricted. In dedicated storage at power plants or remote locations may allow having more limits to those specifications.

Hydrogen can be stored in different ways and procedures, as compressed gas, liquefaction, cryo-adsorbed gas storage in activated carbon, metal hydride storage, carbon nanotube storage, and reversible chemical reactions. In the following table it can be seen some examples of storage density and energy density for various hydrogen storage forms compared to natural gas and biofuels [22].

Table 7: Energy density and density comparison

STORAGE FORM	ENERGY DENSITY		DENSITY
Units	kJ/kg	MJ/m <sup>3</sup>	Kg/m <sup>3</sup>
Hydrogen, gas (ambient 0.1 MPa)	120,000	10	0.090
Hydrogen, gas at 20 MPa	120,000	1,900	15.9
Hydrogen, gas at 30 MPa	120,000	2,700	22.5
Hydrogen, liquid	120,000	8,700	71.9
Hydrogen in metal hydrides	2,000-9,000	5,000-15,000	
Hydrogen in metal hydride, typical	2,100	11,450	5,480
Methane (natural gas) at 0.1 MPa	56,000	37.4	0.668
Methanol	21,000	17,000	0.79
Ethanol	28,000	22,000	0.79

In this case, due to the storage going to be placed inside a boat, the type to be used it is the hydrogen compressed gas form, which it is the most common storage form nowadays in the transportation sector. Standard cylindrical storage tanks uses pressures of 10-25 MPa, and fuel cell vehicles stores are currently in the range of 35-70 MPa. Depending on the pressure hydrogen is being stored, the density varies, but it does not follows the linear process as an ideal gases, as it can be seen in the following graphic (graphic 4) [5].



Graphic 4: Hydrogen and ideal gas density comparison

The tanks for stationary uses are usually made of steel or aluminum-lined steel (TYPE I and II), weight considerations make composite fiber tanks more suitable for vehicle applications (TYPE III and IV) [13] [4].

There are four standard types of hydrogen gas storage tanks depending on the pressure required. Those standard types were developed by the ANSI/AGA standards, NGV2-1998 and NGV2-2000, and have become the key for industry acceptance of high-pressure storage cylinders. ISO standards were developed later in 2009 by the ISO/TS 15869:2009. Although NGV2-2000 has been until nowadays the main ANSI standard for CNG, a review has been done and NGV2-2007 will be published and approved in the following months it will become the new standard. Meanwhile, later in 2014, the new standard about CHG, the HGV-2, was developed and approved by the ANSI standards.

Despite the new standards about CHG have been approved, the tank classification used in the CNG are still being followed, as it have been described in the standards. In the following table (table 8) are described each storing type depending on their pressure and specifications:

Table 8: Hydrogen gas storage tanks types and description

TYPE	MAX. PRESSURE	SPECIFICATIONS
TYPE I	30 MPa	All metal cylinder.
TYPE II	30 MPa	Load-bearing metal line hoop wrapped with resin-impregnated continuous filament.
TYPE III	Vehicle: 70 MPa Stationary: 88 MPa	Non-load-bearing metal line axial and hoop wrapped with resin-impregnated continuous filament.
TYPE IV	Vehicle: 70 MPa Stationary: 88 MPa	Non-load-bearing non-metal line axial and hoop wrapped with resin-impregnated continuous filament.

Nowadays there is a fifth type that is being developed that could lead to a maximum pressure of 100 MPa. It is not really suitable that could be developed higher pressure tanks, because, as it can be seen in the previous graphic (graphic 2), the improvement on the hydrogen density is not high enough.

The main parts of a hydrogen tank can be seen in the following image (Figure 6).

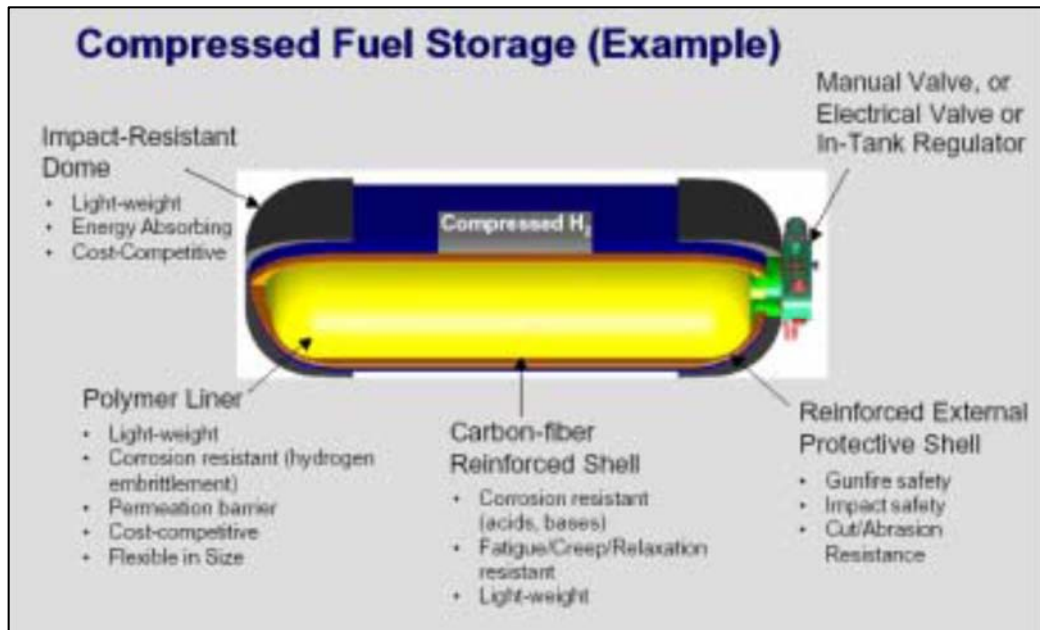
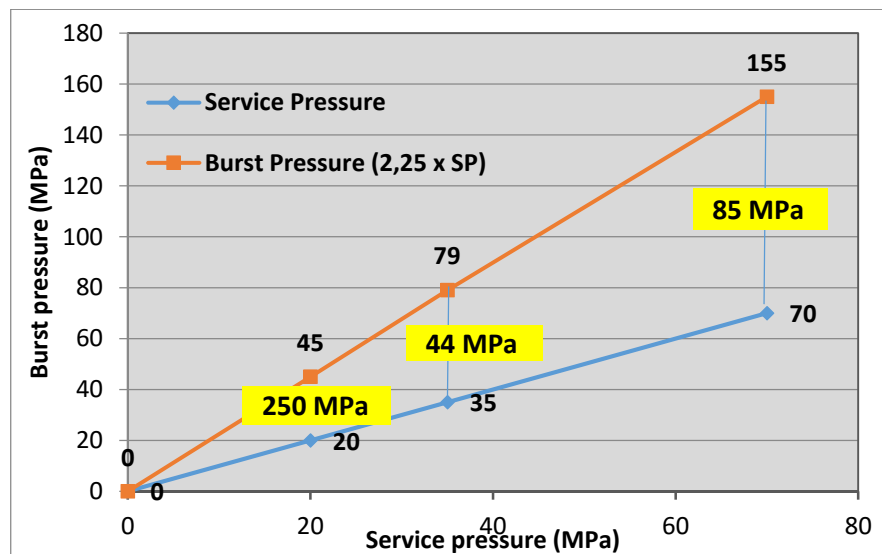


Figure 5: Hydrogen storage tank parts (From TOYOTA MIRAI TECHNOLOGY)

As a way to ensure the pressure inside the tank will not overpass the limits and develop to a problem, the different technologies have a safety measure within development. That safety pressure is the burst pressure and can be seen in the following graphic (graphic 5) [29]:



Graphic 5: Burst pressure depending on service pressure.

## 4.1 Actual use

As a part of the thesis, it has been done a research about the hydrogen storage tank used in the actual commercial fuel cell vehicle, the TOYOTA MIRAI. This is the first commercial vehicle in the world using Fuel Cells as an engine instead of an ICE or Electric batteries [25].

The TOYOTA MIRAI uses two hydrogen storage tanks situated on both sides of the Fuel Cells with a total internal volume of 122.4 l. and the mass of the hydrogen stored is approximately of 5 kg at 70 MPa. The hydrogen storage tanks are of the TYPE IV and are developed using the TOYOTA technology. Are based of three layer structure with the following parts:

- Inner layer: Plastic liner to prevent the hydrogen leakage.
- Middle layer: Carbon fiber reinforced plastic as the main structural element.
- Surface layer: Glass fiber reinforced plastic that protects the outer surface from abrasion.

## 4.2 Tank analysis

In the case that is being studied in this thesis, a hydrogen storage tank of the TYPE IV is needed, because it is the tank type with the highest pressure required with the less possible weight due to their building characteristics. For this reason, some manufacturers that build and sell hydrogen storage tanks in different pressures and volumes have been contacted.

Baltic Yachts provided their study of hydrogen gas storage tank from Ballard Power Systems for the comparison with the other products achieved, also the Toyota hydrogen gas storage technology is being used in the comparison [15].

Hexagon Raufoss provided their three actual hydrogen gas tanks that are in the market and also gave some details about a possible future tank that could be developed [27].

Quantum Technologies hydrogen gas tanks analyzed have been collected from a review from the National Renewable Energy Laboratory of the U.S. Department of Energy in Colorado. Efforts have been made to contact the company for new and more detailed hydrogen gas tanks technology but it has not been possible [21].

The following table shows the different hydrogen storage tanks obtained after the research for the thesis.

Table 9: Hydrogen storage tanks comparison

	Tank Unitary Values					On board Tank Selection									
Company	Working pressure	Tank technology	Geometrics			Weight	Hydrogen			Tanks					
			Diameter	Length	H <sub>2</sub> O Volume		Unit. Tank Weight	H <sub>2</sub> Target	Density (1)	Required Volume	Number of tanks	H <sub>2</sub> Total Volume	Total Tanks Weight	H <sub>2</sub> Storage Total Mass	Specific Weight
	(barg)	(m.)	(m.)	(m³)	(kg)	(kg)	(kg/m³)	(m³)	(Units)	(m³)	(kg)	(kg)	(kg tank / kg/H <sub>2</sub> )	(kg)	
BALLARD	350	TYPE 4			0.2000	100.0	25.0	25.0	1.000	5	1.000	500	25.000	20.000	525.000
HEXAGON RAUFOSS	950	TYPE 4	0.515	2.780	0.2540	365.0	25.0	50.0	0.500	2	0.508	730	25.400	28.740	755.400
	500	TYPE 4	0.580	3.280	0.5300	280.0	25.0	32.5	0.769	2	1.060	560	34.450	16.255	594.450
	700	TYPE 4			0.6250	450.0	25.0	42.0	0.595	1	0.625	450	26.250	17.143	476.250
	700	TYPE 4	0.319	0.906	0.0360	34.0	25.0	42.0	0.595	17	0.612	578	25.704	22.487	603.704
TOYOTA	700	TYPE 4	2 Tanks (60 l. Front, 62.4 l. Rear)		0.1224	87.5	25.0	42.0	0.595	5	0.612	437.5	25.704	17.021	463.204
QUANTUM TECHNOLOGIES	700	TYPE 4			0.2200	100.0	25.0	42.0	0.595	3	0.660	300	27.720	10.823	327.720
	350	TYPE 4			0.3200	90.0	25.0	25.0	1.000	4	1.280	360	32.000	11.250	392.000

Notes: (1) Density at specific working pressure.

### 4.3 Safety

The safety related to hydrogen gas storage is really important because of the pressure and the type of gas stored in it. As it is explained in chapter 4, the standards that have been used until a few years ago for the hydrogen gas storage in high pressure tanks are the standards of the CNG storage, because the main characteristics of both standards are mostly the same. As in both cases the gas stored is a flammable gas, despite natural gas has a more flammable power and a lower percentage mixture with air to produce an explosion, as it can be seen on the table 4. Just with those premises, the security standards of CNG storage are higher than the ones needed on the hydrogen gas storage and were able to be implemented until ISO standards will be approved.

The current designs on the hydrogen gas storage tanks have been based on decades of industrial experience. Those in-service experience, explained in the different CNG standards [4], have been developed from different conditions such as:

- Vehicle service conditions (could be exposed to very severe environments)
  - Temperature extremes (-40 °C to 85 °C)
  - Multiple fills (changes in pressure) → fatigue cracking
  - Exposure to road environments and cargo spillage
  - Vibrations
  - Vehicle fires
- End user requirements
- In-service failures (known failure mechanisms) o abuse
- Collisions
- Manufacturing problems
- Design problems

Those condition could produce different types of failures at an extreme situation, and can be classified in eight different causes:

- Mechanical damage: External abrasion and/or impact.
- Environmental damage: External environment assisted.
- Overpressure: Faulty fueling equipment of faulty cylinder valves.

- Vehicle fire: Faulty PRDs or lack of PRDs; localized fires.
- Plastic liner issues: Manufacturing defects.
- Metal liner issues: Manufacturing defects.

For preventing all possible failures and malfunctions, different tests have been developed in the standardization organizations for being checked during the development of a new product and proving the different safety measures are the appropriate ones.

## 5 Hydrogen refueling

### 5.1 Thermodynamic characteristics

Rapid and high-density refueling is the important for H<sub>2</sub> storage acceptability. The pressure at the tanks during the refueling process is affected by the thermodynamic laws, that determines the H<sub>2</sub> storage density and therefore the range of energy produced in the Fuel Cells [16].

Before an empty compressed hydrogen tank is filled with H<sub>2</sub>, there are some important aspects to know about:

- How hot the tank will become while the hydrogen is being compressed.
- Which is the final pressure.
- How much hydrogen will be inside the tank.

The tank refueling process can be modeled with the first law of thermodynamics. Initially, it can be considered an empty tank with negligible thermal mass and negligible heat transfer from/to the environment. With these considerations, the first law of thermodynamics is simplified to:

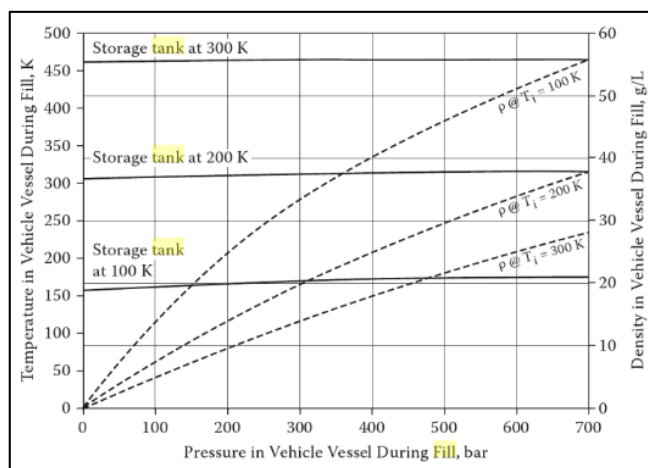
$$(4.1) u_f = h_i$$

Where  $u_f$  is the specific internal energy of the hydrogen inside the tank, and  $h_i$  is the specific enthalpy of the H<sub>2</sub> flowing. The  $h_i$  enthalpy is calculated at the hydrogen station's tank conditions ( $p_i, t_i$ ), assumed constant during the whole process.

$$(4.2) h_i = u_i + p_i \cdot v_i$$

The term  $p_i \cdot v_i$ , named the flow work, it is the heating that happen when gases are forced into a tank.

In the following figure (graphic 6), it can be seen how the density of the hydrogen changes during the refueling process and how the temperature of the gas increases because of the compression. In this figure, it is assumed a refueling process for a tank at an initial pressure of 700 bar, and varying the initial temperatures between 100, 200 and 300 K.

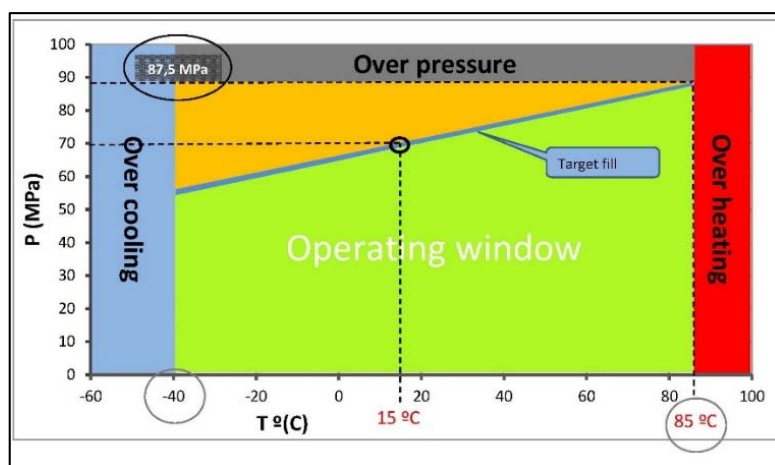


Graphic 6: Temperature and density during the refueling process. (From Klebanoff L. *Hydrogen Storage Technology: Materials and Applications*)

As it can be seen in the figure, if the initial stationed hydrogen is at 300 K, the final temperature of the gas supplied in the tank would be at 460 K, and it can deliver only 28 g/l of hydrogen into the tank. Alternatively, if the initial stationed hydrogen it is at 100 K, the final temperature of the gas supplied in the tank would be at 175 K, and it can deliver only 56 g/l of hydrogen into the tank.

Although there is a big difference in the temperature of the hydrogen delivered, inside the tank the temperature is nearly constant during all the refueling process, the small changes are produced due to the non-ideal behavior of the  $H_2$ , especially in low temperatures. Also it has to be taken care about the heating of the hydrogen gas during the compression process because it can produce internal degradation of the tank surfaces if too high temperatures are reached.

In the process of refueling care has to be taken about the different limits of the storage. It has some limits depending on the temperature and pressure, as it can be seen in the following graphic (graphic 7) from the refueling limits of a 70 MPa hydrogen gas tank [29]:



Graphic 7: Operating window of a 70MPa Hydrogen Gas tank

## 5.2 Procedure

There are two main procedures or options for supplying the hydrogen gas, it can be delivered to the site or it can be generated on-site. As nowadays there is no enough infrastructure to produce hydrogen gas on-site in the different harbours and marinas, the main option should be the delivered to the site [2].

In this case, hydrogen would be delivered as a compressed gas in cylinders using a truck that would drop of the storage tanks for the refueling process using special machinery and then taken again when they are empty. Also, if a really large amount of hydrogen is needed, a tube trailer can be purchased and deliver the hydrogen using pressurised tubes.

A tube trailer with hydrogen tubes at a pressure of 20 to 25 MPa will arrive to the marina. Then, the tube trailer will be connected via a compressor to the hydrogen tanks placed in the boat. That compressor must be placed in the boat for safety and better refueling process.

In the following figure (figure 6) there is a representation of the process of refueling. As it can be seen, to avoid the extra heat produced during the different compression processes, there is a cooling process after each compressor. Before refueling the tube trailer, the hydrogen arrive to the compressor stage at 14 bar and is compressed and cooled to avoid different problems related with the heat produced and to have the maximum amount of energy produced released.

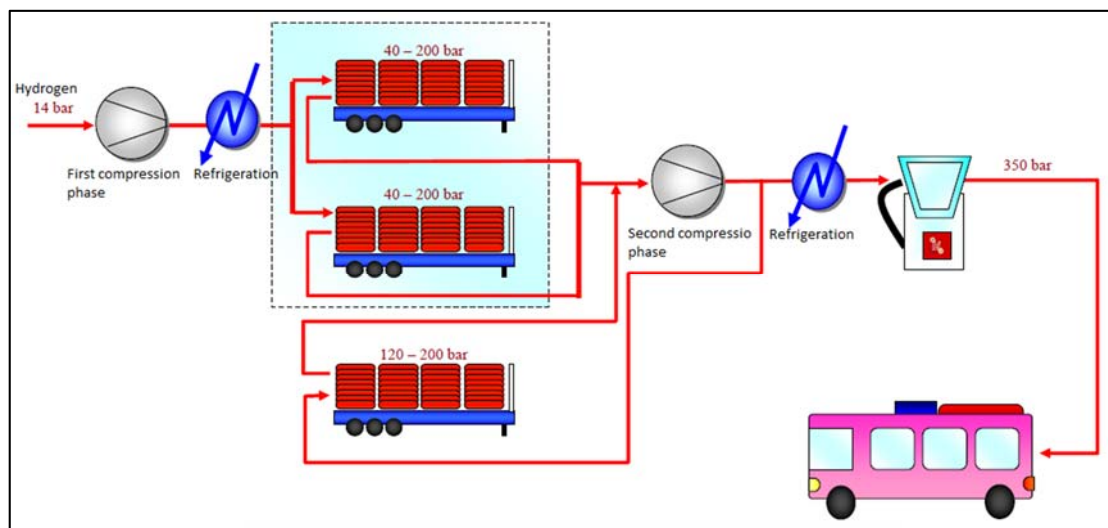


Figure 6: Hydrogen refueling process (From Repsol).

The previous figure (Figure 6), has been received from a Repsol S.A. employee contacted for some information related to the distribution of hydrogen gas in Spain [11].

In a near future, the same technology as the vehicles are using nowadays will be placed in the marinas. Using a hydrogen refueller hydrogen is dispensed to the tank using a flexible hose and nozzle connected to the vehicle tank. In this case the compressor would be placed in the refueling system, not in the boat.

Inside the storage tank at the boat, before the refueling process, the tanks are empty. As they are at a tight environment, during the consumption process they are loosing pressure, due to the deliver of hydrogen to the fuel cells, and at the end they are with just a few particles of hydrogen, what it can be considered as they are empty, without any hydrogen and vacuum pressure.

### 5.3 Infrastructure

For being possible to reach the procedure of not refueling the hydrogen gas tanks with a tube trailer that will arrive to the harbour it is needed to have a vast infrastructure of hydrogen filling stations.

In Europe, on January 2013 a new proposal for a directive was approved in the European Union [8]:

*Proposal for a Directive of the European Parliament and of the Council on the deployment of alternative fuels infrastructure.*

That proposal has the main objective to ensure the stablishment of a minimum infrastructure for the use of alternative fuel in the land, sea and river transport in the whole territory of the EU. In terms of hydrogen fuel, there would be filling stations of public access within a distance of 300 km and all must be operative by the end of 2020.

Apart from that directive, various countries have created different partnerships with governmental departments and the private sector involved to study and develop new projects for the technology. One example is the Project DEMO2013 [20].

### **5.3.1 Project DEMO2013**

Project DEMO2013 it is a project taken place at the new port facilities at Vuosaari Harbour in Helsinki and the main aim is to show the different uses of fuel cell application of their technologies and services on stationary solutions to utility vehicles, working machines and low-power applications. Also the project includes the development of the infrastructure required to the refueling process to those vehicles and machines.

The development of this new project in the new Vuosaari Harbour was part of the Tekes programme 2001-2013, with the main aim to speed the development and application of innovative fuel cell technologies. One of the first programme projects that brought some results was a 20 kW SOFC power plant in Vaasa done by Wärtsilä that has been operating successfully 3,000 hours.

## **6 Hydrogen: Improvement of the A.C. system**

### **6.1 Electrical system**

The electrical system of a boat can change depending on the dimensions of the boat, but the main parts are the same. The yachts from Baltic Yachts produce the electricity between the main engine, with an alternator, and a group of different electrical generators, normally between two to three. The electricity generated passes through two different groups of batteries, one group of 24 V batteries and another group of 240-700 V. high voltage batteries. The electricity generated goes directly to the batteries to prevent problems in case of electricity peaks that could damage any electrical equipment on the boat because the batteries always deliver a constant current of electricity. During the night, one of the biggest consumptions of electricity is the air conditioning system, because almost all the other electrical devices are shut down. Also during the night, in case the main engine is not working, only one of the generator is working, this generator is called a silent generator because of their low noise and vibrations that produces, although not all the vibrations are eliminated and those vibrations produced are transferred to the boat structure. The average amount of electricity required during the night is between 9 and 20 kW depending on the dimensions of the boat and the required consumptions [15].

A way to reduce the electrical consumption produced by the cooling system and also the vibrations and noise produced by the generator is to implement a new system in which using the hydrogen as a cogeneration fuel, producing electricity through the fuel cell system and using the hydrogen consumed by those fuel cells as a refrigerant for the A.C. system. That hydrogen fuel cell system can decrease the needs of electricity by the A.C. system.

#### **6.1.1 The consumptions of the Air Conditioning system**

The A.C. system is one of the largest electrical consumers when it is working, and during the night it is even largest, in percentage, of the total consumption. This big consumption requires that when the boat it is on the shore, the A.C. is connected directly to the shore power. At the dock, the A.C. system draws between 4 and 13 A [28]. When the engine is

working, these amperages are manageable, but under sail or at anchor, there is needed a sizable inverter and the battery banks to support those loads.

The A.C system has an average consumption of 4 kW during the night that represents around a third of the total electrical consumption. In case of using the improved system will decrease highly that consume because only the pump for the water of the A.C. system will be working, and also there will be a production of electricity from the hydrogen fuel cells.

## 6.2 The Air Conditioning system of the studied boat

The A.C. system of the boat analyzed is a chilled water air conditioning which works using a water loop between the chiller and the air handlers of the different cabins instead of using a refrigerant. This system consists of a chiller, located in the engine room, which cools fresh water that is pumped through an insulated piping loop out to the different air handlers located in the living spaces, where the cabin air is cooled. The water loop works delivering water at 7 °C after the compressor, and the return temperature to the condenser is at 10.5 °C, a difference of 3.5 °C<sup>1</sup>.

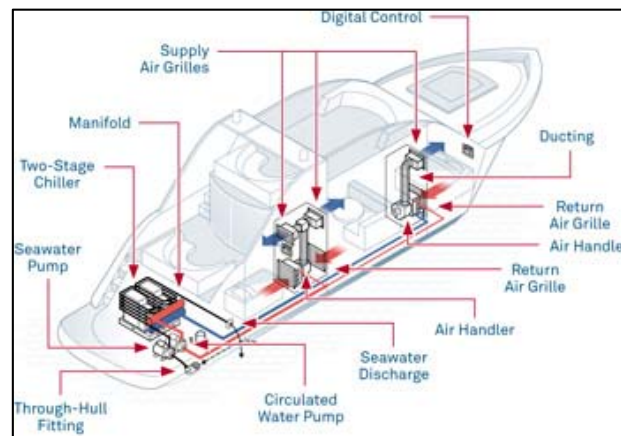


Figure 7: Typical installation of an A.C. system (From Florida Yacht Management)

Nowadays, the way to cool the fresh water is through a condenser unit that produces the exchange with the sea water. Sea water, apart from having a normal constant temperature, it is a source that it is surrounding the boat and with that source there is no need for using a refrigerating gas that could pollute the environment with any leak.

---

<sup>1</sup> Normally the temperature difference at the A.C. system is 5 °C. In this case it is of 3.5 °C and it is explained at the chapter 6.3.2.

The circuit of the sea water inside the A.C. system begins entering to the pipeline from an inlet thru-hull fitting, a special opening that not allows big elements to enter through the pipeline system, followed by a seacock, a special water valve that controls the amount of sea water entering the system. After the valve there is a strainer, where any big particle that could damage the system are hold and cleaned, that stained needs a regular supervision for checking if it is empty to allow a fluent flow of water. Following the strainer, there is the seawater pump, where the pump will be moved to the A.C condenser unit, where the heat exchange is produced with the closed water circuit of the A.C. system. Ones the heat exchange process has finished, the sea water has an overboard discharge again to the sea.

Depending on the size of the boat, for the closed water circuit of A.C system will have a different flow. In the studied case, for a chiller heat exchanger of 42 kW of thermal power is required a flow of 170 l.p.m, or what is the same, a water mass flow of 2.8 kg/s though the water closed circuit pipes [17].

The schematics of the system are can be seen in the following figure.

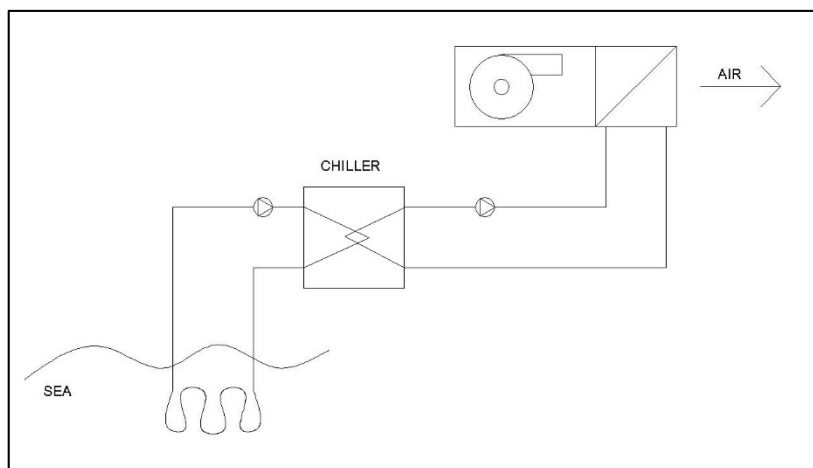


Figure 8: Schematics of the actual A.C. installation.

### 6.2.1 Thermal power

The thermal power of an A.C. system of a boat is the power at the exchanger that measures the amount of heat taken from the closed water circuit, in case we want to produce cold air, or given to the closed circuit, in case the aim is to produce hot air. To understand the strength of the thermal power system, first of all, depending on the region are going to use one units or another, as an example in Europe the units are kW and in U.S.A. the units are BTU/h. here are some calculations as an example to compare it with the thermal power units given

by Baltic Yachts. The main data it is going to be used in those calculations have been taken from the West Marine website [28], having a schematic guide how to design an A.C. system for a yacht.

The different data calculations will be used are for a system with an average thermal power ( $Q$ ) of 16,000 BTU/h. The BTU/h, the abbreviation of British Thermal Unit, is a non-SI energy unit used mainly in English-speaking countries, such as Canada and U.S.A. Using the BTU per hour, BTU/h, is a power unit of heating or cooling, in that case, the conversion to S.I. units is 1 BTU/h equals 0.293 W.

$$(6.1) Q = 16,000 * 0.293 = 4688.16 W = 4.688 kW$$

After the conversion, the average heat power for the A.C. system is 4,688 kW. In the case studied, the average consumption of the A.C. chiller system is bigger because of the dimensions of the yachts designed, those thermal powers can go from 14 kW, for a yacht of 60 feet or 18 meters, to a thermal power of 42 kW, for a yacht of 200 feet or 60 meters [15].

The thermal power, in this cases between 14 kW and 42 kW, is the installed thermal power, when normally the maximum power used during the day normally is lower. During the night, that thermal power is, normally, even lower because different factors, such as the lower temperature, the lack of movement of people between the outside and the inside, and the solar radiation. For this the different calculations it is going to be used the installed power as a thermal power exchange.

### 6.2.2 Energy efficiency

If during the night the consumption of the A.C. system is normally around a third of the total consumption, it is possible to calculate the coefficient of performance of cooling or  $COP_c$  of the installation. The  $COP_c$  of the A.C. system installed is the percentage between the cooling thermal power or heat exchanged from the closed water circuit to the refrigerant ( $Q_c$ ) and the electrical consumption ( $W$ ) of the installation.

$$(6.2) COP_c = \frac{Q_c}{W}$$

The average consumption during the night of a small yacht installation (example data given by Baltic Yachts) is around 9 kW and, as it is said before, the A.C. consumption during the night normally is around a third of that total power consumption. In this case the A.C. system

power consumption during the night it is going to be considered of 4 kW. With that data it is possible to calculate the COP with the equation (6.2):

$$(6.2) \text{COP}_c = \frac{Q_c}{W} = \frac{14}{4} = 3.5$$

Having an installation with a  $\text{COP}_c$  of 3.5 it means that the A.C. installation is a really efficient one.

The  $\text{COP}_c$  of an installation, nowadays, is not the value used to show the cooling energy efficiency of a cooling installation. For this energy efficiency classification, nowadays, are using two rates, the energy efficiency rate, the EER, or the seasonal energy efficiency rate, SEER. Those new energy efficiency classifications are used to classify the different installations depending their efficiency [3]. To calculate the new classifications from the  $\text{COP}_c$ , the equations to use are the following ones:

$$(6.3) \text{EER} = \text{COP} * 3.413$$

$$(6.4) \text{SEER} = \text{COP} * 3.792$$

Using those equations it is possible to calculate the new efficiency rates:

$$\left. \begin{array}{l} \text{COP} = 3.5 \\ (6.3) \text{EER} = \text{COP} * 3.413 \\ (6.4) \text{SEER} = \text{COP} * 3.792 \end{array} \right\} \begin{array}{l} \text{EER} = 3.5 * 3.413 = 11.94 \\ \text{SEER} = 3.5 * 3.792 = 13.70 \end{array}$$

Those new efficiency rates classify the A.C. installation of the yacht as an A+++, this is the highest possible rate that an A.C. installation can achieve. The different classification rates can be seen in the following energy efficiency classification table (table 10) [1]:

Table 10: Energy efficiency classification

	<b>EER</b>	<b>SEER</b>
A+++	$\text{EER} \geq 4.10$	$\text{SEER} \geq 8.50$
A++	$3.60 \leq \text{EER} \leq 4.10$	$6.10 \leq \text{SEER} \leq 8.50$
A+	$3.10 \leq \text{EER} \leq 3.60$	$5.60 \leq \text{SEER} \leq 6.10$
A	$2.60 \leq \text{EER} \leq 3.10$	$5.10 \leq \text{SEER} \leq 5.60$
B	$2.40 \leq \text{EER} \leq 2.60$	$4.60 \leq \text{SEER} \leq 5.10$
C	$2.10 \leq \text{EER} \leq 2.40$	$4.10 \leq \text{SEER} \leq 4.60$
D		$3.60 \leq \text{SEER} \leq 4.10$
E		$3.10 \leq \text{SEER} \leq 3.60$
F		$2.60 \leq \text{SEER} \leq 3.10$
G		$\text{SEER} \leq 2.60$

As it can be seen from the table, the EER and the SEER values obtained from the A.C. installation are higher than the minimum values for the A+++ classification. That difference is produced because the classification for all the A.C systems in the market. That represents

that are using the same classification for systems that are refrigerated by air. In this case of study, the exchange is between water, which is more efficient than with the air.

### 6.3 Use of hydrogen as a cooler for the A.C. system

One application of the fuel cell system studied is to create an exchanger during the transmission process, between the decompression process of the hydrogen gas, after being released from the storage tank, and the fuel cell stacks, where electricity is going to be generated. The fuel cell system is composed by the fuel cell stacks and the hydrogen gas storage tanks.

The idea is to provide enough cold exchange power to work as a part of the A.C. system during the night, taking advantage of the low temperatures reached after the decompression process. During the decompression process the hydrogen gas released from the tank expands diminishing the pressure, from the stored pressure to the ambient pressure, and also diminishing the temperature, reducing their density. For accomplish this process the hydrogen gas consumes heat. This process, due to the small scale of the decompression system used, nowadays it is not possible to take advantage of that heat exchange with the exterior.

The procedure of the decompression of the hydrogen normally is not studied in depth. That lack of study is caused because when the hydrogen moves directly from the hydrogen gas storage tank to the Fuel Cell stocks, the temperature during that process is not really important, it only has to be between the limits of the operational temperature of the fuel cell stocks. In the patent EP 2224519 A1 [18], that involves a design of a prototype of a “*Hydrogen storage vessel apparatus comprising an ionic decompression cell*”, in their section 68 it is explained that during the decompression process the hydrogen loses temperature.

After achieving this change in those state conditions, the hydrogen gas has to be transported to the fuel cell stocks. During that transmission process, it is where the heat exchanger it is going to be placed. The fuel cell stocks have a wide range of operational temperatures, normally between 0 °C and 80 °C, but in cases of the SOFC fuel cells it can be reached maximum temperatures of 1,000 °C [9]. The information of the PEM fuel cell stocks supplied by Baltic Yachts, which are going to be used in this study, can operate between the

temperatures of 2 °C and 60 °C. From that range at the operational temperature, during the transportation process of the hydrogen gas it is possible use some heat from the closed water circuit to increase a little bit the hydrogen temperature at the heat exchanger.

Although the increase of the hydrogen temperature will produce a decrease of the electrical production, because it will produce a decrease of the hydrogen gas density with the consequent decrease of the efficiency in the fuel cell stacks, the A.C. systems inside the boat will require less heat energy to cool down the temperature of the closed water circuit thanks to that previous heat exchanger. That means that both systems will be placed in series, first the hydrogen heat exchange system followed by the A.C. system.

The condenser has a thermometer sensor that measures the temperature of the closed water circuit at the entrance of the condenser. When the exchange process with the hydrogen is taking place, if the temperature target of 7 °C is achieved the condenser will not work and the water from the closed circuit will just pass through it. This process helps to being a safety measure in case during the night the heat exchange with the hydrogen gas stops working, the condenser will start working and cooling down the water from the closed circuit.

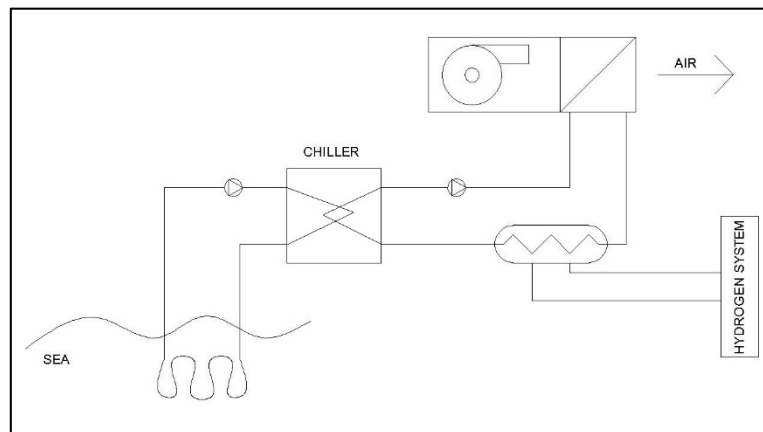


Figure 9: Schematics of the improved A.C. installation.

### 6.3.1 Decompression assumptions

Before the analysis and calculations of the system there are some assumption that have to be done. Those assumptions are required because some of the data information have not been possible to get due to the high technological information required.

The first assumption is that after the decompression of the hydrogen there is a decrease of the temperature. That decrease of temperature is also produced at the decompression process of the natural gas. Depending on the temperature inside the hydrogen gas storage tank the

temperature reached after the decompression can change widely. Normally, the lowest temperature reached after the decompression is -30 °C.

The second assumption is that the temperature reached after the decompression process are those -30 °C. This assumption is done to achieve a maximum range of working heat exchange.

### 6.3.2 Calculations

The calculations are going to be divided into two parts, firstly to calculate the thermal power exchange of the hydrogen and secondly to calculate the flow of fresh water of the closed circuit that can be produced with the thermal power of the hydrogen calculated [24].

One of the assumptions for the calculations of the thermal power exchange of the hydrogen ( $Q_h$ ) is that is going to be considered as an ideal heat exchanger. The equation that is going to be used to calculate the thermal heat power of the hydrogen is the following one:

$$(6.4) Q = \dot{m} * C_p * |\Delta T|$$

Where:  $Q_h$  = heat exchange (kW)  
 $\dot{m}$  = mass flow (kg/s)  
 $C_p$  = heat capacity at a constant pressure (kJ/ [kg\*K])  
 $\Delta T = (T_e - T_i)$  = difference of temperature

That variables change depending on the state of the elements and situation to calculate. In this case, to calculate the  $Q_h$  the variables have the following values:

- The  $\dot{m}_h$  of the hydrogen is 5 kg of hydrogen per night, and the night is considered of having a duration of 8 hours:

$$\left. \begin{array}{l} m_h = 5 \text{ (kg)} \\ t = 8 \text{ (hours)} \end{array} \right\} \dot{m}_h = \frac{0.625 \left( \frac{kg}{h} \right)}{3,600 \left( \frac{s}{h} \right)} = 0.000174 \left( \frac{kg}{s} \right)$$

- The  $\Delta T_h$  is the difference between the exit temperature ( $T_e$ ) and the entry temperature ( $T_i$ ) of the hydrogen during the heat exchange process. In this case it is going to be considered the entry temperature at -30 °C, 243 K, and the exit temperature it is going to be 10 °C, 283 K.

$$\Delta T_h = T_e - T_i = 283 - 243 = 40 \text{ (K)}$$

- The  $C_{ph}$  of the hydrogen depends on the temperature of the hydrogen it is going to use the value at the average temperature between the entry temperature ( $T_i$ ) and the exit temperature ( $T_e$ ). In this case the  $C_{ph}$  it is going to be  $14.12 \left( \frac{kJ}{kg \cdot K} \right)$ .

Now it is possible to calculate the hydrogen heat exchange value from the equation (6.4):

$$(6.4) Q_h = \dot{m}_h * C_{ph} * |\Delta T_h| = 0.000174 * 14.12 * |40| = 0.098 kW = 98 W$$

As a result, the hydrogen heat exchange value is low. To determine if it is enough for the system it is going to be calculated the flow of water that is possible to cool down. That value is going to be compared it with the chiller heat exchanger of 42 kW of thermal power that has a mass flow of 2.8 kg/s.

Before continuing with the calculations, using the equation (6.4) it can be calculated the  $\Delta T$  of the water, using the mass flow of 2.8 kg/s, the  $C_p$  of the water at 10 °C and the thermal power of 42 kW.

$$(6.4) Q_w = \dot{m}_w * C_{pw} * |\Delta T_w| \rightarrow |\Delta T_w| = \frac{Q_w}{C_{pw} * \dot{m}_w} = \frac{42}{4.19 * 2.8} \approx 3.5 K$$

As the target temperature is 7 °C, 280 K, and it is known the entry temperature of the closed water circuit at the hydrogen exchanger has to be higher, the difference of temperature is negative. The higher temperature is going to be:

$$\Delta T_h = -3.5 = T_e - T_i = 280 - T_i \rightarrow T_i = 280 + 3.5 = 283.5 (K)$$

To calculate the flow of water from the closed circuit that could be cold it is going to use the equation (6.4), but in this case the unknown value is the mass flow of the water ( $\dot{m}_w$ ). The different values of the variables are the following ones:

- The water heat exchange,  $Q_w$ , it is going to be the same as the hydrogen heat exchange,  $Q_h$ , because one of the assumptions is that the heat exchange process is ideal.

$$Q_w = Q_h = 0.098 kW$$

- The  $\Delta T_w$  is the difference between the exit temperature ( $T_e$ ) and the entry temperature ( $T_i$ ) of the water during the heat exchange process. As it has been calculated before, the  $\Delta T_w$  it is going to be  $|-3.5| K$ .
- The  $C_{pw}$  of the water depends on the temperature of the hydrogen it is going to use the value at the average temperature between the entry temperature ( $T_i$ ) and the exit temperature ( $T_e$ ). In this case the  $C_{pw}$  it is going to be  $4.19 \left( \frac{kJ}{kg \cdot K} \right)$ .

$$(6.4) Q_w = \dot{m}_w * C_{pw} * |\Delta T_w| \rightarrow \dot{m}_w = \frac{Q_w}{C_{pw} * |\Delta T_w|} = \frac{0.098}{4.19 * |-3.5|} = 0.0067 \left( \frac{kg}{s} \right)$$

As it can be seen the difference between the flow required for the chiller heat exchanger of 42 kW of thermal power installation, 2.8 kg/s, and the flow that the hydrogen is able to cool, 0.0067 kg/s, is really big.

From that difference of the values it is possible to conclude that the hydrogen it is not a possible refrigerant liquid for the chiller heat exchanger of 42 kW of thermal power installation.

To check a the possible solution for this problem, that is increasing the flow of hydrogen for a higher thermal power exchange, it is going to calculate the required flow of hydrogen to achieve the target for the chiller heat exchanger of 42 kW of thermal power installation. The equation to use is the same as in the previous calculations, the equation (6.4). In this calculations, first of all is necessary to calculate the water heat exchange,  $Q_w$ , using the target flow for the installation, 2.8 kg/s.

All the constants are going to be the same, because the difference of temperatures and the heat capacity at a constant pressure of both liquids are the same.

$$(6.4) Q_w = \dot{m}_w * C_{pw} * |\Delta T_w| = 2.8 * 4.19 * |-3.5| = 41.61 \text{ kW}$$

Using the value obtained for the water heat exchange,  $Q_w$ , as the hydrogen heat exchange value,  $Q_h$ , it is possible to calculate the hydrogen mass flow required to stop operating the chiller heat exchanger and use the hydrogen heat exchanger.

$$(6.4) Q_h = \dot{m}_h * C_{ph} * |\Delta T_h| \rightarrow \dot{m}_h = \frac{Q_h}{C_{ph} * |\Delta T_h|} = \frac{41.61}{14.12 * |40|} = 0.0737 \left( \frac{kg}{s} \right)$$

With that hydrogen flow, the total amount of hydrogen required during the whole night would be of around 2,122 kg of hydrogen.

With that mass flow of hydrogen it is possible to achieve the target, but that means using around 400 more mass flow of hydrogen than the required to run the hydrogen fuel cell system.

## 7 Fuel cell systems

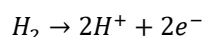
### 7.1 Types

The fuel cells can be divided depending the electrochemical reaction that occurs inside the cell, depending on the different electrolyte used. The electrolyte used also determine the operating temperature of the fuel cell. The operating temperature of the fuel cell is very important, because in low temperature fuel cells all the fuel that enters to the fuel cell has to be pure hydrogen. In those low temperature fuel cells, the catalyst of the anode, mainly platinum, has a great corrosion due to the carbon monoxide (CO), and even methane (CH<sub>4</sub>). The different types of fuel are explained widely at the Fuel Cell Handbook edited by the U.S. Department of Energy [9].

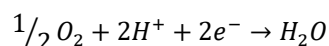
#### 7.1.1 PEFC

[9] Polymeric electrolyte membrane fuel cells, or PEFC, are a type of fuel cells that are able to generate, efficiently, high power densities. This technology has the achievement that has made the technology potentially attractive for different applications, such as mobile and portable fuel cells. Also, this is technology used in the different transportation applications. This technology differentiates from the other fuel cell technologies because uses a solid phase membrane as an electrolyte. Because of that membrane, PEFC can operate at low temperatures, allowing a faster startup process than the higher temperature fuel cells. This type of fuel cells can reach an electrical efficiency about 60% with an operating lifespan of about 8,000 hours. Proton Exchange Membrane fuel cells, or PEM, are one type of PEFC. The electrochemical reactions that occurs at the anode and the cathode are the following ones:

ANODE REACTION



CATHODE REACTION



The different components of a typical PEFC stack are:

- The ion exchange membrane.
- An electrically conductive porous backing layer.
- An electro-catalyst at the interface between the backing layer and the membrane.

- The cell interconnectors and flowplates that deliver the fuel and oxidant to reactive sites via flow channels and electrically connect the cells.

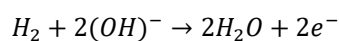
### 7.1.2 AFC

[9] Alkaline Fuel Cell, or AFC, were one of the first modern fuel cells to be developed, used to provide on-board electric power at the Apollo space vehicle. The AFC have an excellent performance compared to other fuel cells due to its active O<sub>2</sub> electrode kinetics and flexibility to use a wide range of electro-catalysts. During normal operation, the electrolyte circulates continuously, which has several advantages over the immobilized system such as:

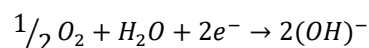
- No drying-out of the cell occurs because the water content of the caustic electrolyte remains constant inside the stock.
- No heat exchanger is required because the electrolyte itself works as a cooling liquid inside each cell.
- Accumulated impurities are mainly concentrated in the circulating stream and can easily be removed.
- The electrolyte prevents the build-up of gas bubbles between electrodes and electrolyte as they are washed away.

This type of fuel cells normally have an operative temperature between 65 °C and 220 °C, can reach an electrical efficiency about 60% with an operating lifespan of about 5,000 hours. The electrochemical reactions that occurs at the anode and the cathode are the following ones:

#### ANODE REACTION



#### CATHODE REACTION

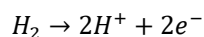


### 7.1.3 PAFC

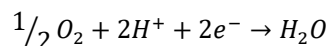
[9] Phosphoric Acid Fuel Cell, or PAFC, was the first fuel cell technology to be commercialized. Most of the power plants build with PAFC stocks are in 50 and 200 kW of capacity, but larger plants have been build. The electrochemical reactions occur on highly dispersed electro-catalyst particles supported on carbon black and platinum alloys are used as the catalyst in booth electrodes.

This type of fuel cells normally have an operative temperature between 150 °C and 200 °C, and can reach an electrical efficiency about 40% with an operating lifespan of their components of about 40,000 hours. The electrochemical reactions that occurs at the anode and the cathode are the following ones:

#### ANODE REACTION



#### CATHODE REACTION

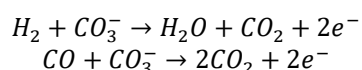


### 7.1.4 MCFC

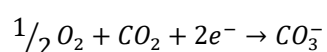
[9] Molten Carbonate Fuel Cell, or MCFC, normally operate at the highest operating temperature possible because is needed to achieve sufficient conductivity of the carbonate electrolyte. There is a benefit associated of using this high operating temperature and is that noble metal catalysts are not required for the electrochemical oxidation and reduction processes at the cell. MCFC are being developed for natural gas and coal-based power plants for industrial and electrical utility.

This type of fuel cells normally have an operative temperature between 600 °C and 700 °C, and can reach an electrical efficiency about 50% with an operating lifespan of their components of about 12,000 hours. The electrochemical reactions that occurs at the anode and the cathode are the following ones:

#### ANODE REACTION



#### CATHODE REACTION

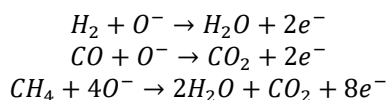


### 7.1.5 SOFC

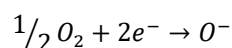
[9] Solid Oxide Fuel Cell, or SOFC, have a solid, non-porous metal oxide electrolyte. Due to their high operating temperature, between 600 °C and 1,000 °C, places stringent requirements on its materials. The cell is constructed with the electrolyte between two porous electrodes. When an oxygen molecule contacts the cathode it acquires electrons. The oxygen ions diffuse into the electrolyte material and migrate to the other side of the cell, the anode. Those oxygen ions encounter the fuel at the anode and react catalytically, giving of water, carbon dioxide, heat and electrons. The SOFC for stationary generation can have a power

between 2 kW to 100s MW of capacity. This type of fuel cells normally have an electrical efficiency about 60% with an operating lifespan of their components of about 40,000 hours. The electrochemical reactions that occurs at the anode and the cathode are the following ones:

#### ANODE REACTION



#### CATHODE REACTION



### 7.1.6 Fuel cell types summary

The following table is a way to summarize all those five types of fuel cell stacks comparing their different characteristics:

Table 11: Fuel cell characteristics

	PEFC	AFC	PAFC	MCFC	SOFC
<b>Electrolyte</b>	Hydrated polymeric ion exchange membranes	Mobilized or immobilized potassium hydroxide in asbestos matrix	Immobilized liquid phosphoric acid in SiC	Immobilized liquid molten carbonate in $LiAlO_2$	Perovskites (Ceramics)
<b>Electrodes</b>	Carbon	Transition metals	Carbon	Nickel and nickel oxide	Perovskite and perovskite / metal cermet
<b>Catalyst</b>	Platinum	Platinum	Platinum	Electrode material	Electrode material
<b>Interconnect</b>	Carbon or metal	Metal	Graphite	Stainless steel or nickel	Nickel, ceramic or steel
<b>Operating T° (°C)</b>	0 – 80	65 – 220	150 - 200	600 - 700	600 – 1,000
<b>Charge carrier</b>	$H^+$	$OH^-$	$H^+$	$CO_3^{2-}$	$O^-$
<b>External reformer for hydrocarbon fuels</b>	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell designs
<b>External shift conversion of CO to hydrogen</b>	Yes, plus purification to remove trace CO	Yes, plus purification to remove trace CO and $CO_2$	Yes	No	No
<b>Prime cell components</b>	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic
<b>Product water management</b>	Evaporative	Evaporative	Evaporative	Gaseous product	Gaseous product
<b>Product heat management</b>	Process gas + liquid cooling medium	Process gas + electrolyte circulation	Process gas + liquid cooling medium or steam generation	Internal reforming + process gas	Internal reforming + process gas

## 7.2 Fuel cell installation

In this study case, the fuel cell to use is suggested by Baltic Yachts [15]. It is a PEM fuel cell stack from the company called Ballard. The fuel cell is from the “FCvelocity – 9SSL” PEM fuel cell models, which is designed to perform in rugged conditions and scalable depending on the different operating requirements. The different stocks are available from 4 kW to 21 kW. The characteristics of the FCvelocity – 9SSL PEM fuel cell models are:

Table 12: PEM fuel cell characteristics

FCvelocity – 9SSL PEM CHARACTERISTICS	
Type	Proton exchange membrane
Maximum current	300 A
Fuel composition (H <sub>2</sub> purity)	> 95% H <sub>2</sub>
Oxidant composition	Compressed ambient
Storage temperature (°C)	-40 to 60
Start-up temperature (°C)	> 2
Fluid inlet temperature (°C)	2 to 68
External ambient (°C)	-25 to 75

Those previous characteristics are the same for all the different models of the PEM fuel cell. The fuel cell chosen produce 10.5 kW of rated power, with a voltage of 35 V and at a current of 300 A. The total weight of this fuel cell system is 50 kg.



PRODUCT SPECIFICATIONS						
Rated Power [kW] <sup>1</sup>	3.8	4.8	10.5	14.3	17.2	21.0
DC voltage (at 300A) <sup>1</sup>	12.8	16.0	35.0	48.0	57.4	70.2
Mass (with no coolant) [kg]	7.1	7.2	10.7	13	15	17
Stack core length [mm]	92	104	174	220	255	302
Stack core width [mm]	760	760	760	760	760	760
Stack core height [mm]	60	60	60	60	60	60

Figure 10: Fuel cell product specifications

## 8 Standards

The main standard organizations that propose and develop the different standards and regulations are the ISO, the International Organization for Standardization [13], and the ANSI, the American National Standards Institute [4]. The ISO organization is an international non-governmental organization which regulates the standards of the 164 member countries, and the ANSI coordinates the United States standards with the ISO standards so that the American products can be used worldwide. The main objective of the standards are to facilitate world trades by providing common standards between nations. Nearly 20,000 standards have been developed for regulating from manufactured products and technology to food safety, agriculture and healthcare.

In this thesis have been told about different standards from both organizations. As it has been explained, the hydrogen standards have been developed in previous years, and because of that situation, for a long time, the CNG standards have been used as the standards.

The main CNG standards used are the following ones:

- ANSI
  - o NGV2-1998
  - o NGV2-2000
  - o NGV2-2007
- ISO
  - o ISO 11439
  - o ISO/DIS 16923.2
  - o ISO/PC 252

The main Hydrogen Gas standards used are the following ones:

- ANSI
  - o HGV2-2014
- ISO
  - o ISO/TS 15869:2009
  - o ISO/CD 19884
  - o ISO/TC 197

## 9 Conclusion

The conclusions of this thesis are different depending on the area of study.

First of all, hydrogen is a high power energy density fuel that has been used for decades. This energy density can be stored in high pressure tanks due to their high compressibility factor. This compressibility factor allows hydrogen to be compressed to high pressures that allows large amounts of gas being stored. The final specifications for the hydrogen gas storage tank system, after adding the fuel cell system weight of 50 kg, are the following ones:

In this case, the decision should be done by the designers of the boat, because there are two tanks that could be useful. The first one is tank of Quantum Technologies that operates at a pressure of 35 MPa. This storage tank can operate at a stationary operational process during six nights and half of the seventh night, with a total weight of 442 kg, divided into 4 different tanks. The second tank is the tank of Hexagon Raufoss that operates at a pressure of 50 MPa. This storage tank can operate at a stationary operational process during six nights and almost all of the seventh night, with a total weight of 644.45 kg, divided into two different tanks

Those 200 kg of difference have a huge impact on the dimensioning of the boat, but using the 4 tank system of Quantum Technologies, which not all the tanks have to be used at the same time, brings the possibility for a safety tank in case there is any electrical generation problem with the generators and the main engine.

In the heat exchange process analyzed in this thesis it has been seen that with the flow of hydrogen that passes through the heat exchanger it is impossible to reach the target temperature of the cold water from the closed circuit of 7 °C. The required flow of hydrogen to achieve that target should be around 400 times the current hydrogen flow.

Although the target of removing the use of the A.C. condenser unit during the night has not been reached, there is the possibility of cooling down the water from the closed circuit and help the A.C. condenser not to work at the maximum power required. That solution is possible because the hydrogen heat exchanger is situated in series before the A.C. condenser. This possible solution to reduce the energy consumption required for the A.C. system. At the same time, if there is less energy required by the electrical system of the boat it will require less energy generation from the fuel cell. This decrease in the energy generation would require less hydrogen consumption. This decrease of the consumption will produce an increase of the autonomy of the hydrogen stored, allowing the system work more hours.

In the fuel cell stocks, as it has been seen, the amount of electricity generated, 10.5 kW, is enough for the average consumption of the boat, 9 kW. This situation cause an increase of the electricity stored at the different batteries. At the same time, could represent a decrease of the electrical generation requirements, with an increase of the autonomy of the fuel stored for the engine and the generators. If there were more time for this study, the specifications of the fuel cell system could be optimized to the electrical demand during the night to achieve the zero demand of fuel during the night, using only the fuel cell system, and allowing the remove of one of the generators, in case there is more than one generator.

Future improvements in this field depends on the technological improvements achieved during the following years. Those improvements will be, mainly, from the fuel cell part, having smaller and more efficient fuel cell stocks. Another improvement that could be suitable for study could be the use of the heat consumption of the hydrogen during the decompression process. During this process, the hydrogen consumes heat, and if this heat consume could be possible to use, there would be another way to produce a heat exchange and having cold.

The patent explained in the chapter 6.3, is a patent to build a fuel cell system in only one piece, placing the fuel cell stocks inside the hydrogen tank.

The standards related to CHG are being developed nowadays. As a future improvements, those standards will be modified or reviewed. Those new standards will help the improvement of the sector by having a specific regulation for them.

To conclude, the hydrogen fuel cell technology is, nowadays, achieving a high performance of development that requires a constant search and knowledge of the new products and improvements done.

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