

**UNIBERTSITATEKO MASTERRA:**

**Industria Ingeniaritza**

# **MASTER AMAIERAKO LANA**

***KARBONORIK GABEKO ORDEZKO ERREGAIEN  
ERABILERAREN ANALISIA ERRAIL ETA ITSAS  
APLIKAZIOETAN ERREAKTORE MEMBRANEN  
BIDEZ/  
ANALYSIS OF MEMBRANE REACTOR  
APPLICATION IN RAIL AND MARINE  
APPLICATIONS WITH ZERO CARBON  
ALTERNATIVE FUELS***

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## LABURPENA:

Negutegi efektua gizarteak aurre egiteko duen erronka handienetako bat da. Hidrogenoa, bere energia dentsitate altua izanik eta dituen Negutegi Efektuko Gasen emisio eza dela eta, ibilgailuetan energia produzitzeko ordezko aukera interesgarritzat hartu da. Hala ere, hidrogenoaren biltegitratzeak eta garraiatzeak zientzialarientzat erronka handia suposatzen dute. Ikerlan honen helburua ibilgailuan hidrogenoan eta hidrogenoa dakarten beste erregaietan oinarritzen diren energia sortzeko teknologiak alderatzea bilatzen du. Lan honetan aipatzen diren teknologiak Barne Errekuntzako Motorrak, Mintz Erreaktoreak eta Erregai Pilak dira. Ibilgailuan hidrogenoaren biltegitratzea erronka nagusienetako bat izanik, honentzako irtenbide aiposatuak aztertu ziren. Gainera, lortutako datuetatik abiatu eraginkortasun orokorrak kalkulatu dira. Kalkuluen ondoren, zehaztu da sistemarik eraginkorrena ibilgailuan energia produzitzeko eta hidrogenoa gordetzeko, amoniakoan oinarritutako biltegitratze sistema gehi membrana erreaktore eta erregai pila. Ikerketa honetan Karbono Bahiketa eta Biltegitratze sistemak ere kontutan izan dira proposatutako irtenbideak hala eskatu duenean.

## ABSTRACT:

Global warming is one of the main challenges that society is facing. Hydrogen, because of its high energy density and zero greenhouse gases (GHG) emissions when used to generate energy, is one of the most interesting alternatives to generate energy onboard transportation means. On the other hand, hydrogen presents important challenges in the time of its transportation and storage. This review aims to compare different onboard energy generation systems based on hydrogen and other hydrogen carriers with and without membrane reactors. The technologies that are presented in this work are Internal Combustion Engines (ICE), Membrane Reactors (MR) and Fuel Cells (FC). How to store the hydrogen onboard is also a challenge and therefore, it was analysed which were the best solutions for it. After considering global efficiencies it was determined that storing hydrogen in the form of ammonia combined with a membrane reactor to generate hydrogen and to feed it to a fuel cell to generate electricity was the most efficient system among the proposed ones considering the energy efficiency and the hydrogen carrier storage. In this study, exhaust gas after treatments and Carbon Capture and Storage (CCS) systems were also included when needed to compare different propulsion systems.

## RESUMEN:

El cambio climático es uno de los mayores retos a los cuales la sociedad está haciendo frente. En el caso del hidrógeno, debido a su gran densidad energética y a que no tiene emisiones de Gases de Efecto Invernadero durante su oxidación, hacen que esta sustancia resulte una de las alternativas de producción de energía embarcada más interesantes para la comunidad científica. Pese a ser una de las alternativas más interesantes, su almacenamiento a bordo o transporte suponen grandes retos. Esta revisión bibliográfica tiene como fin comparar distintas tecnologías que produzcan energía a bordo a partir de hidrógeno u otros portadores de hidrógeno para medios de transporte pesado haciendo uso o no de reactores de membrana. De esta manera, las tecnologías que se presentan en este trabajo son los Motores de Combustión Interna, los Reactores de Membrana y las Pilas de Combustible. Teniendo en cuenta que el almacenamiento y transporte del hidrógeno supone uno de sus mayores retos, también se han analizado las mejores soluciones para ello. Tras considerar las eficiencias globales de cada sistema de producción de energía embarcada las cuales se han obtenido a partir de las referencias revisadas, se concluye que el sistema de mayor eficacia de producción de energía embarcada a partir del hidrógeno es el

almacenamiento químico en forma de amoníaco y la producción de hidrógeno puro mediante reactores de membrana y la generación de energía a partir de pilas de combustible. Este estudio también incluye sistemas de post-tratamiento de gases de combustión y sistemas de almacenaje y captura de carbono cuando las soluciones energéticas los han requerido.

**HITZ GAKOAK:** Hidrogenoa, energia, biltegitratzea, membrana erreaktorea, barne errektuntza motorrak eta erregai pila.

**KEY WORDS:** Hydrogen, energy, storage, membrane reactors, internal combustion engines and fuel cell.

**PALABRAS CLAVE:** Hidrógeno, energía, almacenamiento, reactores de membrana, motores de combustión interna y pilas de combustible.

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## ACRONIMS

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|        |  |
|--------|--|
| GHG    | Greenhouse gases                         |
| ICE    | Internal Combustion Engine               |
| MR     | Membrane Reactor                         |
| FC     | Fuel Cell                                |
| CCS    | Carbon Capture and Storage               |
| GMST   | Global Mean Surface Temperature          |
| PEMFC  | Proton Exchange Membrane Fuel Cell       |
| STP    | Standard Temperature and Pressure        |
| SMR    | Steam Methane Reforming                  |
| LOHC   | Liquid Organic Hydrogen Carriers         |
| NOx    | Nitrogen Oxides                          |
| MeSR   | Methanol Steam Reforming                 |
| PM 2.5 | Particulate Matter of 2.5 µm of diameter |
| SIE    | Spark Ignited Engine                     |
| CIE    | Compression Ignited Engine               |
| DF     | Dual Fuel                                |
| SCR    | Selective Catalytic Reactor              |
| EGR    | Exhaust Gas Recirculation                |
| DMFC   | Direct Methanol Fuel Cell                |
| PAFC   | Phosphoric Acid Fuel Cell                |
| AFC    | Alkaline Fuel Cell                       |
| MCFC   | Molten Carbonate Fuel Cell               |
| SOFC   | Solid Oxide Fuel Cell                    |
| NSG    | No Sweep Gas                             |
| WGS    | Water Gas Shifting                       |
| PSS    | Porous Stainless Steel                   |

# 1. INTRODUCTION

---

Global climate change has been nowadays one of humanity's main challenges. The global mean surface temperature (GMST) keeps increasing every year[1]. In the baseline scenarios, in which no mitigation actions are taken in the following decades, global warming could increase by 3.7°C to 4.8°C by 2100 compared with pre-industrial levels[2].

Global warming is driven by the emissions of GHG. Carbon dioxide is the main anthropogenic GHG accounting for 68% of the total anthropogenic emissions in 2018 and most of it comes from fossil fuel combustion and industrial processes[3]. The principal source of these emissions is electricity and heat generation which accounted for 42% and transport for 22% of total emissions in 2018[4].

As mentioned, transportation is one of the main sources that is warming up the planet's atmosphere. Different solutions have been proposed to reduce emissions coming from this sector. Electric vehicles such as cars and buses have become one of the most popular solutions to reduce these noxious gases[5], although their benefit depends on the source of the electricity. Their low energy demand compared to heavy means of transportation has made possible the use of electric batteries, but this solution might not be feasible for all transportation sectors. While an average car has a power demand of 134.22 kW[6], a bulk carrier ship may have a mean break power demand of 6472.67 kW[7], 48 times more power than a car, usually driven by diesel engine. The Diesel engines; in spite of having high efficiency, durability and reliability, are considered as one of the main contributors to environmental pollution[8]. This has brought to great concern in the different organizations in charge of environment control. In case of automotive vehicles for example, the EU is considering to ban diesel engine vehicles' sales by 2030[9].

Apart from suggesting electric batteries as a solution for transportation, researchers have come up with other solutions to reduce the emissions coming from the transport sector.

In the last decade, with the aim of reducing CO<sub>2</sub> emissions, hydrogen has gained considerable importance among different fields of energy and technology, for instance, energy storage and transport sector are the main ones[10]. Nonetheless, its storage together with its production are still challenging for scientist[11]. There are two ways in which hydrogen can be stored, physically or chemically. Physically refers to store it by compression forces or through liquefaction, while chemically refers to store it as another chemical compound combined with other atoms. In this second storage technology, ammonia and methanol are found. These hydrogen storage systems can be considered green fuels depending on the origin of the hydrogen they are storing. Nevertheless, considering methanol as a green fuel is still a source of debate because of its carbon content and consequent GHG emissions when oxidized.

There are two different ways to make use of the energy of these fuels. On the one hand, there are ICE which obtain the energy from these hydrogen carriers through a combustion process. On the other hand, there are fuel cells together with membrane reactors. For this second way, firstly the membrane reactors are responsible for obtaining purified hydrogen and later the fuel cell converts the hydrogen's chemical energy into electricity. In this review we want to study the use of proton exchange membrane fuel cell (PEMFC) coupled with a membrane reactor.

Hydrogen is the most abundant element in the universe and it has one of the highest energy densities, whose lower heating value is 121 MJ/kg[12]. Indeed, 324g of hydrogen have the same energy as 1 kg of gasoline. Even so, the principal drawbacks of this energy vector<sup>1</sup> are that it is rarely found in its simplest form in nature and its state at standard temperature and pressure (STP)

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<sup>1</sup> An energy vector is a tool that allows the transportation and storage of energy[209]



is gaseous. On this account hydrogen production and transportation are still challenges for scientists[13].

Hydrogen is a widely demanded substance in the global market. The main industrial applications are: 33% in oil refining, 27% in ammonia production, 11% in methanol production and 3% in steel production via the direct reduction of iron ore. In addition, it is expected to increase the demand for methanol and ammonia production processes in the next years[14][15]. Not only that, but also the transport sector is about to become part of the market of this colourless gas which will have consequences on this demand.

Nowadays, most of the produced hydrogen comes from the steam methane reforming method (SMR). SMR method produces around 48% of industrial hydrogen[16][17]. Another common process is coal gasification, which produces 18% of the global production.

These methods have something in common, the GHG that are released during the process. With the SMR, hydrogen is produced through the exposure of natural gas with heat and steam. In this practice, methane reacts with water vapour producing carbon monoxide, carbon dioxide, and hydrogen molecules[11][15]. Water electrolysis has the potential to meet the zero-emissions target, but the cost of this production technology is two to four times higher than the previously stated methods[19]. Figure 1 shows the different routes that are available nowadays to obtain hydrogen. Hydrogen feedstocks and energy production routes can be combined differently to produce hydrogen.

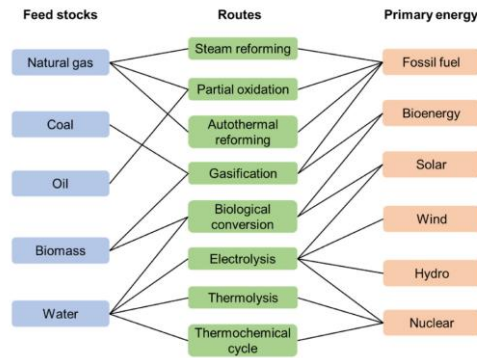


Figure 1 – Primary energy sources, feedstock and routes for hydrogen production [19]

## 1.1. HYDROGEN’S PRODUCTION AND COLOUR CODING

Due to the emissions of carbon dioxide and carbon monoxide in most of the hydrogen production methods, the hydrogen used as fuel in the transportation or industrial sectors cannot be directly considered as a carbon-free fuel. The cleanness of hydrogen can be determined by the emissions of the process. A colour is assigned to the process based on the origin of the feedstock.

The colour coding used so far is green, blue and grey, but other ways to classify the produced hydrogen have recently been proposed[14]. For the original coding, this is the meaning for each colour:

- Green hydrogen is produced from renewable energy via the electrolysis of water in order to meet the zero-emission target.
- Blue hydrogen is produced from fossil fuels accompanied by CCS systems.
- Grey hydrogen refers to the hydrogen coming from hydrocarbon-based fuels that emit CO<sub>2</sub>. This is the hydrogen coming from the SMR process.

Nonetheless, scientists are coming up with new ranges to classify each hydrogen production process based on its emissions[17][18]. If hydrogen is going to be the new energy solution for various means of transportation it is important to ensure the cleanness of its production.

Another challenge to consider is the storage of hydrogen. Hydrogen's state at STP is gaseous, this makes its volumetric energy density lower compared to other fuels and therefore needs to be made more energy dense[13]. Studies have determined that it's not efficient to store pure hydrogen[22][23]. Other solutions such as hydrogen carriers where a compound is formed by hydrogen atoms and carbon or nitrogen atoms have been proposed to make good use of this energy vector.

The aim of this review is to provide the reader with the necessary information to compare different power systems for heavy means of transport using hydrogen as primary energy source in different energy vectors. One locomotive example and a bulk carrier example have been used for analysis. The information given in this work is based on descriptive and qualitative research. Therefore, extended literature review has been done to obtain the necessary data that have been used in simplified calculations in order to have an overall picture of the available possibilities with zero carbon fuels that have hydrogen as origin.

## 2. HYDROGEN CARRIERS

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While hydrogen production is a challenge for scientist, its transportation and storage are still a teaser as well. Transportation refers to the transportation of the fuel to supply regions away from the production place but also refers to the transportation of the fuel when it is used during the displacement. This section is intended to analyse different hydrogen storage systems. Hydrogen can be stored physically or chemically.

Many are the solutions that scientists are coming up for hydrogen storage. For instance, Liquid Organic Hydrogen Carriers (LOHC) are also a field which scientific efforts are going for[24]. LOHC are chemical compounds in which hydrogen atoms, carbon atoms and oxygen atoms are combined in liquid or semi-solid states. These substances store and release hydrogen through catalytic hydrogenation and dehydrogenation processes[24]. Their high hydrogen storage capacity ( $>56 \text{ kg H}_2/\text{m}^3$ [25]) make these carriers one of the best hydrogen storage systems.

The most common LOHC are Cyclohexane–Benzene, Perhydro-N-ethylcarbazole–N-Ethylcarbazole, Methylcyclohexane–Toluene or Decalin–Naphthalene among others[25]. Nevertheless, these LOHC are expected to perform as energy storage systems when electricity production is higher than the demand and are not going to be considered in this review.

The graphs shown in this section are based on the gathered data that is included in Table 1. Different properties about several ways of hydrogen storage systems are shown in the table. The storage efficiency of a hydrogen carrier is measured by the hydrogen storage capacity per volume of carrier; the more hydrogen is contained within a volume, the better is the carrier.

All the references that helped to collect this information are shown as well in the table. The software Engineering Equation Solver has been also used to fulfil the data in the table[26].

Several properties are compared to determine which storage system or carrier fits best a heavy means of transportation. For instance, their energy content per volume unit and hydrogen density per carrier volume are a matter of interest. Therefore, aspects such as hydrogen content in carrier volume or the consumed energy for each conversion process are gathered in Figure 2 and Figure 3.

The more hydrogen is contained within a determined volume, the more efficient is the storage system. In addition, the less energy is consumed during the conversion the more economically and energetically interesting will result. For example, compressed hydrogen has the lowest energy consumption per kg carrier, but also the lowest hydrogen volumetric density. In fact, more hydrogen is contained in a given amount of water or gasoline than in pure liquid hydrogen (at 1 bar and -252,87°C); 111 kg/m<sup>3</sup>, 83 kg/m<sup>3</sup> and 71 kg/m<sup>3</sup> respectively[27]. Whereas liquefied ammonia has the highest hydrogen content per carrier volume and has the second lowest conversion energy consumption. It is also important to point out that, unlike ammonia, the methanol's state at STP is liquid and this fact gives this carrier an advantage compared to other carriers. Another downside of pure hydrogen is that hydrogen gas doesn't follow the equation of ideal gas as it deviates from the result when compression occurs and it occupies more space than what the equation calculates[27].

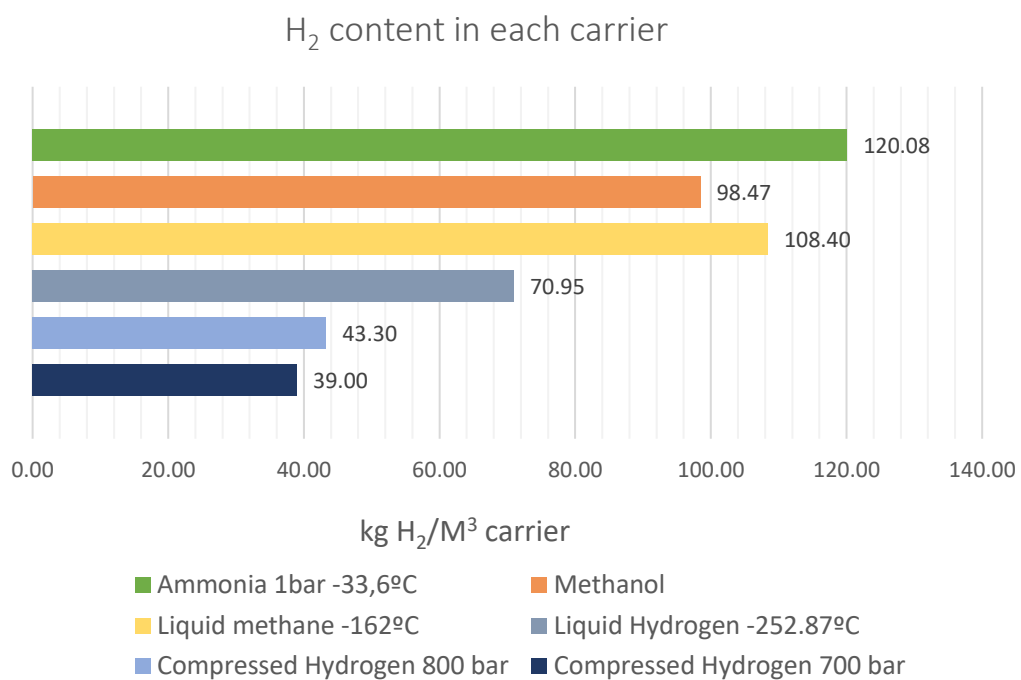


Figure 2 - Hydrogen content H<sub>2</sub> kg/m<sup>3</sup> carrier

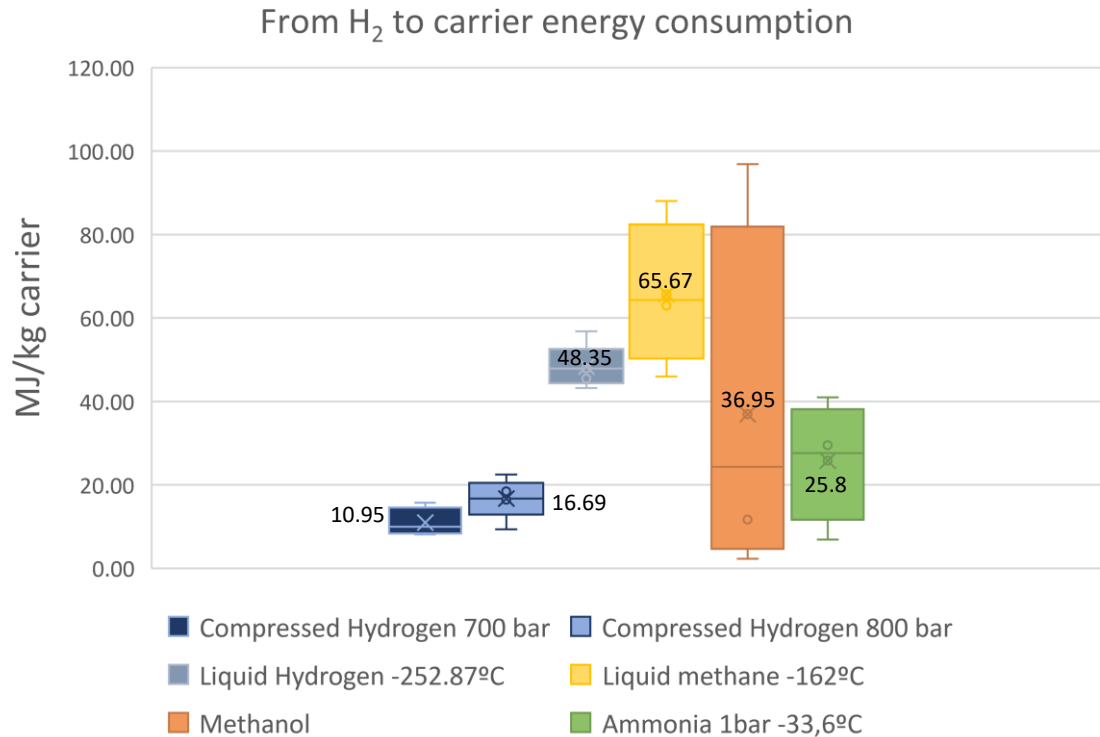


Figure 3 - From H<sub>2</sub> to carrier energy consumption MJ/kg carrier

In Figure 3 we can observe a big dispersion in case of energy consumption per carrier for Methanol and lower dispersion for methane and ammonia. The sources to obtain the values differ in a significant manner between them, not being feasible to summarize in one unique value. Data variation applies for methanol, liquefied methane and liquefied ammonia. For the case of methanol the used sources are [28][29][30][31][32][33]. For the case of liquefied methane the references that were used for this part are [29][28][34][35][36][37][38]. Finally, for the case of liquefied ammonia the sources used were [28][27][29][39][40][41][42][43]. The main reasons of this divergence can be considered in the process used to obtain the carrier, being in many cases industrial processes where energy accounting of process differs notoriously between them. Therefore, few conclusions can be drawn out of this graph. Nevertheless, for the rest of the hydrogen storage systems some notes can be taken as liquefied ammonia seems to be less energy demanding than methanol or liquefied methane.

On the whole, considering the volumetric energy density and the energy required to get the H<sub>2</sub> carrier, the most interesting hydrogen carriers are: liquefied ammonia and methanol. This paper aims to compare zero-emission onboard power generation system, and since methanol is composed of hydrogen and carbon atoms, when it comes to the end-use, carbon dioxide is emitted. This situation leads to considering Carbon Capture Systems to avoid GHG emission to atmosphere, which will require extra energy consumption and space in the transport system. On the other hand, liquefied ammonia doesn't need any CCS system which, as a result, requires less energy and space demand (although it might demand exhaust gas after-treatment system in case of ICE). This paper will be focused on liquefied ammonia and methanol as hydrogen carriers for onboard energy production.

Table 1 - Hydrogen storage systems and hydrogen carriers. Apart from the shown sources, Engineering Equation Solver (EES) was used to obtain densities and compression energies

|                                | Density<br>kg/m <sup>3</sup> | Gravimetric E.<br>density MJ/kg LHV | Volumetric E.<br>density GJ/m <sup>3</sup> | Hydrogen content<br>H <sub>2</sub> mol/carrier mol | Hydrogen content<br>H <sub>2</sub> kg/ carrier kg | Hydrogen density<br>kg H <sub>2</sub> /m <sup>3</sup> carrier | From H <sub>2</sub> to carrier energy<br>consumption MJ/kg carrier | Sources                              |
|--------------------------------|------------------------------|-------------------------------------|--|--|---|---|--|--------------------------------------|
| Compressed<br>Hydrogen 700 bar | 39.00                        | 118.80                              | 5.76                                       | 1.00   | 1.00  | 39.00   | 9.00   | [35][28] [22] [27]<br>[44][45][46]   |
|                                |                              |                                     | 10.00                                      |  |   |   | 15.76  |                                      |
|                                |                              |                                     | 4.90                                       |  |   |   | 8.09   |                                      |
| (Average)                      | 39.00                        | 119.39                              | 6.89                                       | 1.00   | 1.00  | 39.00   | 10.95  |                                      |
| Compressed<br>Hydrogen 800 bar | 43.30                        | 118.80                              | 10.50                                      | 1.00   | 1.00  | 43.30   | 9.36   | [35][28][27][46]                     |
|                                |                              |                                     | 9.93                                       |  |   |   | 22.50  |                                      |
|                                |                              |                                     | 5.20                                       |  |   |   | 16.43  |                                      |
| (Average)                      | 43.30                        | 119.39                              | 8.54                                       | 1.00   | 1.00  | 43.30   | 16.69  |                                      |
| Liquid Hydrogen                | 70.95                        | 118.80                              | 7.20                                       | 1.00   | 1.00  | 70.95   | 56.80  | [35][28][47][22]<br>[27][31][39][48] |
|                                |                              |                                     | 10.10                                      |  |   |   | 45.48  |                                      |
|                                |                              |                                     | 6.40                                       |  |   |   | 47.90  |                                      |
|                                |                              |                                     | 8.00                                       |  |   |   | 43.20  |                                      |
|                                |                              |                                     | 10.50                                      |  |   |   |  |                                      |
|                                |                              |                                     | 8.51                                       |  |   |   |  |                                      |
| (Average)                      | 70.95                        | 119.39                              | 8.45                                       | 1.00   | 1.00  | 70.95   | 48.35  |                                      |
| Liquefied methane              | 420.00                       | 54.00                               | 23.52                                      | 2.00   | 0.25  | 108.03  | 88.00  | [34][35][28][29]<br>[36][38][37]     |
|                                | 500.00                       | 55.60                               |  |  |   | 108.78  | 63.00  |                                      |
|                                | 423.10                       |                                     |  |  |   |   | 46.00  |                                      |
|                                | (Average)                    | 447.70                              | 54.80                                      | 23.52  | 2.00  | 0.25  | 108.40   |                                      |
| Methanol                       | 792.00                       | 22.70                               | 17.97                                      | 2.00   | 0.13  | 99.00   | 2.30   | [28][29][30][33]<br>[31][32]         |
|                                | 786.30                       | 19.90                               |  |  |   | 98.30   | 11.70  |                                      |
|                                |                              |                                     |  |  |   | 98.28   | 96.85  |                                      |
|                                | (Average)                    | 789.15                              | 21.30                                      | 17.97  | 2.00  | 0.13  | 98.47  |                                      |
| Ammonia 1bar<br>-33,6°C        | 682.30                       | 18.65                               | 12.72                                      | 0.18   | 0.18  | 120.08  | 6.90   | [28][27][29][40]<br>[39][41][42][43] |
|                                |                              |                                     |  |  |   |   | 41.00  |                                      |
|                                |                              |                                     |  |  |   |   | 29.50  |                                      |
| (Average)                      | 682.30                       | 18.65                               | 12.72                                      | 0.18   | 0.18  | 120.08  | 25.80  |                                      |

### 3. CARBON CAPTURE AND STORAGE

Carbon capture and storage is considered one of the solutions to avoid carbon dioxide emissions to the atmosphere. Therefore, many industrial sectors are thinking of including a CCS system in their activity. Some of these activities include electricity generation and transportation[49].

During a combustion process or a steam reforming process of a hydrocarbon GHG are released. In order to avoid these emissions carbon dioxide is stored instead of being released to the air. This storing process requires extra energy consumption to liquefy the carbon dioxide as its state at STP is gaseous. The required space for this system is also a challenge to face.

Regarding the hydrogen carriers that have been proposed in the previous section, a CCS system will have to be included for the cases in which methanol is used. The need to include a CCS system gives an advantage to ammonia, because the separation of hydrogen from nitrogen doesn't produce any CO<sub>2</sub> or CO gases, which consequently reduces the extra energy and volume demand. Comparing between both, while the required volume of an ammonia based propulsion system is the volume to supply the necessary energy demand; apart from the volume corresponding to the MR, the volume of a methanol powered system is bigger because of this CCS system. Nevertheless, the truth is that even if CO<sub>2</sub> and CO gases are not produced during the ammonia combustion process, noxious gases such as NO<sub>x</sub> are released which will lead to include also an exhaust gas after-treatment system and partial emissions of those noxious gases that if they are not correctly eliminated, could offset the benefits of not emitting GHG. These NO<sub>x</sub> abatement system are already in operation with diesel engines, although will require modifications to adapt to ammonia combustion characteristics.

In case of Marine transportation, the International Maritime Organization Annex VI regulation 13 for NO<sub>x</sub> emissions. This regulation has a variable Nox emissions limit dependent on engine speed.and in some cases requires exhaust gas after treatment to meet the NO<sub>x</sub> limit[50].

Table 2 - Emissions corresponding to each carrier and power system.<sup>2</sup>

|  | Methanol      |             | Liquid Ammonia |             |
|--|---------------|-------------|----------------|-------------|
|  | SMeR          | ICE         | Decomp.        | ICE         |
| CO <sub>2</sub> production kg/ kWh                       | 0.281[51][52] | 0.334[53]   | -              | -           |
| NO <sub>x</sub> production kg/ kWh                       | -             | Regulations | -              | Regulations |
| CO <sub>2</sub> storage tank L [54]/ kWh                 | 0.386         | 0.458       | -              | -           |
| CCS energy consumption kWh/stored kg CO <sub>2</sub>     | 0.908         |             |                |             |
| CCS energy consumption of the total energy demand % [55] | 26%           | 30%         | -              | -           |

<sup>2</sup> This data was calculated based on the average emissions of each carrier and process and with the tank volume/storing quantity volume ratio divided by the total energy demand of the transport system.

The carbon capture and storage process has been carried out in industrial levels where it has been demonstrated that works[56]. The challenge is to obtain a technology that can compact all the steps into one single process and solve the question of what to do with the captured CO<sub>2</sub>.

For both ways in which methanol is going to be used a CCS system must be included. Therefore, literature research has been done to collect information about onboard carbon capture and storage systems. The International Renewable Energy Agency mentions[57] how this possibility has already been thought about by companies that suggest that the produced CO<sub>2</sub> when generating hydrogen onboard could be carried back to land after a journey.

Before this CO<sub>2</sub> is stored, previous selective separation must be done in order to store as much carbon dioxide as possible. According to A.Garc [58], there are four main types of carbon dioxide separators which have been used in the maritime sector: ammine-absorption, carbonate looping, adsorption and electro-methanol. Most of them are based on an ammine-absorption technology.

Twenty seven onboard post combustion CCS projects are being carried out nowadays, which most of them suggest liquefaction of restored CO<sub>2</sub> as storing solution[57]. This suggests that even though this technology is far from its maturity, efforts coming from governments and companies are directed to improve the feasibility of this technology.

Apart from the technologies mentioned above, membranes have also started to be used for this purpose[58]. Ionada Carbon Solutions LLC Inc. [59] that is working on these CCS systems has affirmed that their Hollow Fibre Membrane Contactor Reactor is able to achieve a carbon capture up to 99%. Most of the projects that are being developed to sequester emissions coming from the maritime sector are destined to natural gas powered shipping[57]. Considering methanol as a fuel for this sector is something recent and therefore few studies have been found who integrate both technologies in one vessel.

According to L.Hyunyong et al. [60], it was analysed the carbon capture and storage of the steam reforming of methane and methanol, the carbon storage efficiency was about 70% with a cogeneration efficiency of 63.32%. It was noted that this storage efficiency could be raised up to 95%, but this would require high energy consumption and therefore the cogeneration efficiency would fall to 54.03%.

Nevertheless, not all studies show the same feasibility prospects, S.Fang et al. [61] determined that achieving up to 80% of emission reduction was infeasible. This review added that if a carbon neutral target is to be achieved by the maritime sector, carbon capture and storage may not be a suitable solution.

Therefore, in order to obtain an approximate volume requirement for the CO<sub>2</sub> storage tank, calculations were done with the gathered information to get some numbers that afterwards conclusions could be drawn. These results are shown in Table 2. It was assumed that the storage efficiency would remain at 70%, which would mean that the propulsion system couldn't be considered as emission free. It was also considered that the best storage system was the liquefied one, and a tank/liquid volume ratio was obtained from Lee et al.'s work[54]. In case of GHG release to atmosphere there is as strong debate if these emissions could be later balanced or offset via other sources of carbon storage accounting to a final value of zero GHG emissions, but this debate is out of the scope of this paper.

Another point to mention in this section is the harmful gases that are produced during the combustion of ammonia. It was mentioned that no CO<sub>2</sub> emissions were related to the combustion of this carrier and perhaps ammonia could seem like a perfect option as a fuel for internal combustion engines, but reality has shown that during its combustion gases more noxious than CO<sub>2</sub> or CO for the atmosphere are released[15]. These gases are denominated NO<sub>x</sub> and refer to

nitric oxides (NO), nitrogen dioxide (NO<sub>2</sub>) and nitrous oxides (N<sub>2</sub>O). They are produced when nitrogen atoms react with oxygen[62]. The non-combusted ammonia is also harmful for the atmosphere as it can react with other compounds found in the air and produce more GHG. In case of N<sub>2</sub>O, its equivalent GHG effect compared with CO<sub>2</sub> is estimated to be 298 kg CO<sub>2</sub> for each kg of N<sub>2</sub>O[63], what makes easily understand the need of its elimination before emitting to the atmosphere.

The company Ionada Carbon Solutions LLC Inc. is also working on NO<sub>x</sub> treating devices to reduce as much as possible these emissions[64]. It claims that their technology removes up to 97% of the nitrogen oxides. In order to treat these gases properly an exhaust gas treatment device must be included.

Ammonia is also one of the main sources for Particulate Matter 2.5 formation in the atmosphere. It reacts with acidic species producing inorganic aerosols that afterwards produce this PM<sub>2.5</sub> and increase its concentration[65].

Fuel spills are also part of the everyday problems in the marine sector. According to Kass et al. [66] this sector is no stranger to fuel spills as this accidental releases occur during refuelling, collisions, or sinking. In the case of ammonia, serious environmental impacts are associated with small releases. For the case of methanol, its high partition coefficient dissolved this fuel rapidly into the seawater which result toxic for the environment and damages the marine life. Therefore, technologies and methods are currently being used to avoid these releases.

In conclusion, carbon capture and storage seems a promising solution to avoid carbon emissions to the atmosphere of the maritime transportation according to Lee et al.[55]. Nevertheless, Fang et al.[61], Eleni et al.[67] and García et al. [58] state that this technology still needs to reach its maturity and become more accessible. Captures of 73% have been demonstrated by García et al. [58] but for an specific situation they suggest that further research is still to be done.

L.Hyunyong et al. have stated [60] that even if a carbon capture and storage technology is introduced in the power generation system, in order to achieve zero-emissions, alternative fuels such as green hydrogen should be used. Taking into account the reviewed references, if CCS has to be used, free carbon emissions vessels are not a feasible and future technology and development will determine whether it is feasible or not.

Finally, for this study the considered approximate occupied volumes corresponding to the storage of carbon dioxide are 0.386 L/kWh for the methanol's steam reforming process and 0.458 L/kWh for the combustion of the methanol where L corresponds to the volume for the tank and kWh is the energy demand of the means of transport. The energy consumption will also be a factor to consider as it will have consequences on the final efficiency of the power system, the more energy consumes the CCS the lower will be the global efficiency of the system. According to Lee et al. [55], the energy consumption of an onboard CCS system is 3.27 GJ/ton CO<sub>2</sub> which equivalently results to be 0.908 kWh/kg CO<sub>2</sub> as shown in Table 2.

## **4. INTERNAL COMBUSTION ENGINES**

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The Internal Combustion Engine (ICE) is a thermal machine capable of burning H<sub>2</sub> in pure condition and any of the other carriers considered in this study. Depending on the type of carrier studied, the development stage of the ICE is different.

Part of the aim of this review is to analyse the performance of ICEs when using non-traditional fuels such as methanol, ammonia and hydrogen. In case of synthetic fuels, the performance of ICE can be very similar to the use of traditional hydrocarbons and does not pose a technological



challenge. Whereas, for H<sub>2</sub>, ammonia and methanol, combustion performances result different due to their combustion and ignition velocities and therefore their usefulness in ICEs will be briefly analysed, pointing the main performance characteristics.

Energy efficiency, emissions of each type of fuel and the available market solutions will be highlighted. From a technological point of view, from the three energy carriers previously mentioned, methanol burning solution would be the technologically most mature one. H<sub>2</sub> and ammonia are in a development phase with some scarce samples in the market in case of H<sub>2</sub>.

## 4.1. METHANOL

Methanol could see application in ICE in the form of pure fuel or blended with other fuels in different forms. In case of pure fuel, methanol can be used in Spark Ignited engines (SIE) or in compression ignited engines (CIE) in which it has to be blended with other fuels in dual fuel cycle due to its high auto-ignition resistance. In Dual Fuel (DF) cycle, a small amount of diesel fuel is injected to the combustion chamber where it ignites due to high pressure and temperature. This diesel ignition ignites the mixture of methanol and air.

In case of SIE, the methanol has many positive attributes which makes it to be considered a good fuel[68]. These attributes are shown in Table 3.

*Table 3 – Methanol’s positive attributes*

| Methanol properties and effects on engine performance |   |  |
|---|---|--|
|   | Properties                                  | Effects on engine performance  |
| 1   | High latent heat of vaporization            | Cools air-fuel mixture and increase density  |
| 2   | High molars expansion ratio                 | Heat losses and friction work decrease   |
| 3   | Low combustion temperature                  | Reduces NO <sub>x</sub> formation  |
| 4   | High hydrogen to carbon ratio               | Reduces CO <sub>2</sub> formation  |
| 5   | High flame speed                            | Fast combustion  |
| 6   | Liquid at standard temperature and pressure | Easy to storage  |
| 7   | High octane number                          | High autoignition resistance and low tendency to detonation. More stable than other fuels. |

Methanol enables notable efficiency increase comparing with other fuels in SIE. From a thermodynamic point of view, this efficiency increase can be attained via higher compression ratio due to reduced auto-ignition capability and reduced adiabatic flame temperature, decreasing heat loss during combustion. The higher latent heat of vaporization will increase charge air density and the volumetric efficiency in the engine. This will cool the charge air and as a consequence NO<sub>x</sub> emissions will be also reduced[69].

The ICE will require a specific system to supply methanol to the engine. The volumetric density content is lower than diesel or gasoline fuel, hence to supply same energy; fuel supply system in engine will have to double the fuel flow rate to supply same energy in same time period. Comparing with traditional ICE burning gasoline or diesel oil, when using methanol, the engine materials will have to be adapted to the properties of Methanol (specially elastomeric materials), not representing this a real challenge with the actual technology level and knowledge[68]:

To end with the brief analysis of the employment of methanol in SIE, it could be said that due to high auto-ignition resistance of methanol, the SIE is the only option to burn pure methanol without any kind of blending or combination with other types of fuels [30]. This means that in case of CIE, it will be completely necessary to blend it with other type of fuels with higher auto-ignition capability.

Considering the methanol engine field application, there are already market available solutions in marine applications for two stroke and four stroke engines. In case of two stroke engines, there are already several samples of engines running in methanol since 2016 with accumulated running hours on methanol alone exceeding 120,000 hours as MAN Energy states[70]. The engines run in dual fuel mode, i.e., methanol with ignition by diesel fuel. The diesel oil injected as pilot fuel to ignite the mixture accounts approximately 6% of the total energy consumed by the engine.

In case of four stroke engines, the solutions available in the market have not accumulated so much operational experience and the more representative sample could be the Wärtsila 32 engine. This engine model works also in dual fuel mode, hence, needs diesel pilot injection for working.

This engine is available in several sizes in the market which vary depending on their rated power. The rated powers account from 3480 kW to 9280 kW and their corresponding engine volumes are  $46.39 \text{ m}^3 = [(A=5.570) * (D=2.345 + F=1.155) * (C=2.380)]$  and  $89.031 \text{ m}^3 = [(A=8.041) * (D=2.120 + F=1.210) * (C=3.325)]$  respectively.

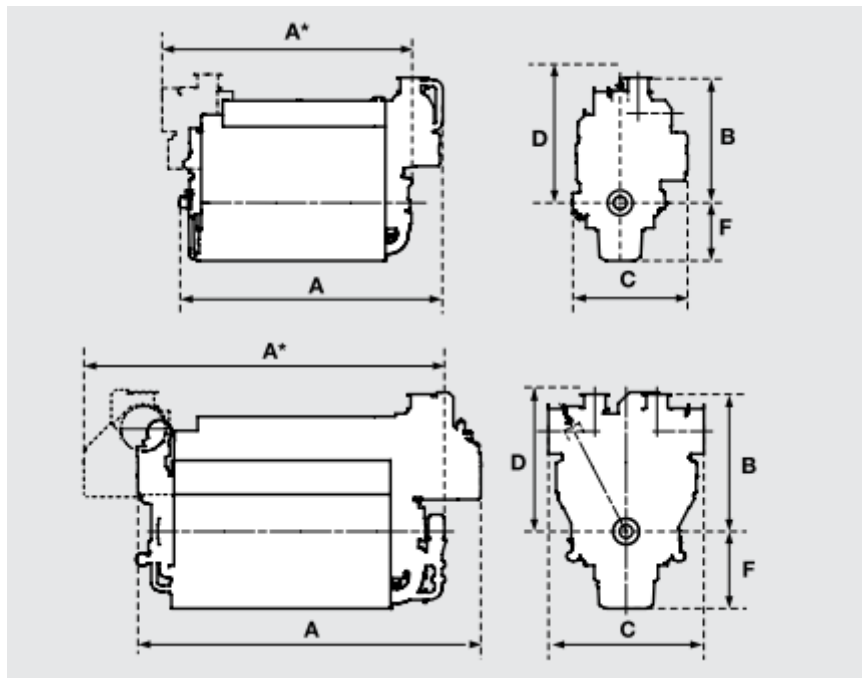


Figure 4 – Dimensions of the methanol combustion engine [71]

In order to compare the sizes of the engines, fuel cells and membrane reactors, the engine volume energy demand ratio was calculated. The specification document for Wärtsila 32 doesn't provide such information, because in fact, the energy demand is linked to the means of transportation and its everyday duty. Therefore, to obtain an energy demand, it was considered the energy demand of the chosen bulk carrier which will be shown in "Section 8. Transport application". In one of the possible routes of the ship, the corresponding energy demand for this bulk carrier is 50,429 GJ, that is,  $1.4 \cdot 10^7$  kWh (with a rated power of 14976 kW). Therefore, for an engine that is able to supply a power demand of 9,280 kW, the energy demand corresponding to a bulk carrier where this engine is installed would be 31,248.74 GJ, that is,  $8.68 \cdot 10^6$  kWh. As a result, the methanol combustion engine's dimension given in L divided by the energy demand in kWh of the means of transportation is 0.01425 L/kWh for the 46.39 m<sup>3</sup> engine and 0.0102 L/kWh for the 89.031 m<sup>3</sup> engine as shown in Table 4.

Table 4 – Engine volume/Energy demand ratio

| Engine volume Energy demand ratio |                |   |             |
|-----------------------------------|----------------|---|-------------|
| Dimension m <sup>3</sup>          | Rated power kW | Energy demand of the means of transport kWh | Ratio L/kWh |
| 46.39                             | 3480           | 3.26E+06                                    | 0.01425     |
| 89.031                            | 9280           | 8.68E+06                                    | 0.01025     |

As far as the authors' knowledge, there are no public data available of energetic ratios of diesel oil and methanol for this engine model. The engine maker claims reductions of NOx of 50% and similar reduction for filter smoke number (indirect indication of smoke and particle emissions)[71].

Regarding the efficiency of an internal combustion engine that uses methanol as a fuel, firstly it will depend on whether it is a SIE or a CIE. Based on the MAN Energy Solutions catalogue for dual fuel mode combustion system [72], after calculations it was determined that the efficiency of a methanol internal combustion engine was 51.86%; slightly smaller than the diesel one 53.6%. These results are shown and compared with the efficiencies for other fuels in Table 6.

In this line, it is becoming more and more common to build new vessels that are methanol ready for possible future retrofits. This means that vessel structure and systems are prepared to be later adapted to methanol use (like fuel tanks, in characteristics and volume).

## 4.2. LIQUID AMMONIA

Ammonia as a fuel has poor combustion characteristics due to its low propagation speed, high ignition delay time, narrow flammability limits and low flame radiation and temperature [73]. It has also a higher ignition energy requirement compared to fossil fuels, what makes it more suitable to be used in SIE or in case of a CIE, combined with a high reactivity fuel that will act as combustion precursor [74]. It could be also combined with other fuels to enhance combustion performance, a small addition of H<sub>2</sub> increases the flame speed and the engine performance, increasing cycle to cycle stability [75].

In case of using diesel fuel as high reactivity fuel in dual fuel mode, it is interesting to minimize diesel fuel amount in order to minimize CO<sub>2</sub> emissions. It has been observed that reliable ignition could be obtained with injection values as low as 3.2% of the total energy in cycle, making CO<sub>2</sub> emissions very low and negligible in case of using organic origin bio-fuels. The tendency observed with pilot injection has been that ignition delay increases for smaller diesel fuel pilot amounts [76]. This has to be considered in time of adjusting the pilot injection quantity and timing.

Due to its low flame speed and high ignition delay time, the use of ammonia in ICE is focused in slow speed engines, two stroke engines or high power and low speed four stroke engines. With this in mind, Liu et al. carried out simulations of a marine two stroke engine with diesel as pilot injection in pre-chamber for pre-mixed combustion. The results suggest that although increasing, NO<sub>x</sub> values would be still within Marine Tier II limits. The only emissions of CO<sub>2</sub> would be from pilot injection and the best performance of engine was obtained with liquid injection of ammonia in the cylinder [77]. It is necessary to remark that CO<sub>2</sub> emissions would come also from the combustion of cylinder oil unless carbon free lubricating oils are developed.

Regarding regulated pollutant emissions in marine environment, NO<sub>x</sub> emissions would have to be addressed. In order to meet marine emissions Tier III limits, the use of Selective Catalytic Reactors (SCR) would be necessary. The use of SCR for exhaust after-treatment would lead to simultaneous reduction of NO<sub>x</sub> and ammonia reductions being feasible its application on board. The reducing agent would be ammonia that would be already available on board as fuel [78]. This SCR are already available in the market and their energy consumption is negligible compared with the CCS systems[79].

Regarding the efficiency of the combustion of this fuel, four sources were considered in order to obtain this information. According to the Korean Register R&D Division [80] efficiency corresponding to the combustion of ammonia through an internal combustion engine would be around 50% and would remain equal for both cases of SIE and CIE. Whereas, Martins et al. considered in their study that this efficiency was around 40% [81]. The Ammonia Energy Society's webpage [82] determined that the efficiency for this combustion process would remain between 35% and 40%. Finally, Chiong et al.'s [83] work was analysed who affirmed that the efficiency would stay close to the 30%.

Taking into account what's said in the previous paragraph, it was considered that the efficiency corresponding to the combustion of ammonia in a ICE would be around 38.75% which is the average of the previous efficiencies.

Regarding the available market solutions for this system, in case of two stroke engines burning ammonia, there is already one engine maker with a clear timeline for an ammonia two stroke engine in the market. MAN Energy has planned 2024 as the year for the first delivery of an ammonia burning engine to ship yard [84]. Therefore, there was no more information found about the dimensions of an ammonia combustion engine. Another engine maker, Wärtsilä, has not fixed any date but is already testing ammonia four stroke engines with plans to commercialize in a near future [85].

### **4.3. HYDROGEN**

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Hydrogen has some important properties to be used in ICEs as an additive. Its very high combustion speed (much higher than petrol) improves the combustion of other fuels even at low fractions (less than 5%). This is beneficial for fuels which burn slowly, such as ammonia.

When the percentage of hydrogen is high or when it is burned on its own (pure), the higher adiabatic flame temperature generates a high quantity of NO<sub>x</sub>, so it is common to inject water as a means to reduce the maximum temperature, especially when supercharging is used. One of the problems of hydrogen is its potential for auto-ignition, as the activation energy (of a spark) required for ignition is very low (0.01 mJ). [81]

Jalundar and Karunamurthy [86] summarized H<sub>2</sub> properties and effect on engine performance that are reflected in Table 5:

*Table 5 – Hydrogen properties and effect on engine performance*

| H <sub>2</sub> properties and effects on engine performance |                              |   |
|---|------------------------------|---|
| Properties  | Effect on engine performance |   |
| 1   | High octane number           | The compression ratio can increase to improve power output                                    |
| 2   | High flame speed             | High power output even at the leanest conditions  |
| 3   | High adiabatic temperature   | Improves combustion efficiency  |
| 4   | Diffusivity                  | Facilitates the formation of air and hydrogen mixture. Avoids or minimizes unsafe conditions. |
| 5   | High calorific value         | Reduces fuel consumption  |
| 6   | High range of flammability   | Helps in running the engine at the leanest condition  |
| 7   | Minimum ignition energy      | Even the smallest electrical leakage can cause a fire. Very unstable.                         |
| 8   | High flame temperature       | Improves efficiency   |
| 9   | Low density                  | More fuel must be supplied to occupy the combustion space and obtained the required output    |

Looking at Table 5 and, comparing H<sub>2</sub> engine with fossil fuel engines it can be deduced that H<sub>2</sub> fuelled engines: are better suited for direct injection in order to increase efficiency (property 8), will perform better with higher speed engines (property 2) and will have higher NO<sub>x</sub> emissions (property 8). At the same time, measures to avoid fires would have to be included in the engine because of its minimum ignition energy, regarding this property it results more risky than other fuels (property 7)[87].

NO<sub>x</sub> emissions increase might be a problem in many cases due to regulations. In order to reduce NO<sub>x</sub>, exhaust gas after-treatment and water injection in combustion chamber might be possible solutions. Exhaust Gas Recirculation (EGR) has also been considered for NO<sub>x</sub> reduction and has provided good results and important NO<sub>x</sub> reductions [88][89][90][91].

The development of H<sub>2</sub> commercial engines is in an advanced stage with some samples available in the market and many examples of engines in the final step prior to entering commercialization. In this way, BeHydro is commercializing its Dual Fuel engine with an energy replacement ratio of fossil fuel with H<sub>2</sub> close to 80%. In case of MAN Energy, they are already supplying dual fuel

engines for a tug boat with a pilot injection of diesel oil down to 5% of total energy[92]. These engines are using SCR for reduction of NO<sub>x</sub>.

In Japan, an alliance of some engine makers has plans to deliver whole range of marine engines burning H<sub>2</sub> for 2025, going from high-speed SIE engines to two stroke diesel cycle engines burning H<sub>2</sub> in dual fuel cycle[93].

Table 6 shows the summary of the part corresponding to internal combustion engines using methanol, ammonia and hydrogen as combustion fuels.

*Table 6 – Thermal efficiencies for each of the combustion engine and used fuel.*

| Fuel     | Efficiencies             | Two Stroke Market Solution | Four Stroke Market Solution | Expected   | Volume Energy Demand ratio L/kWh |
|----------|--------------------------|----------------------------|-----------------------------|--|----------------------------------|
| Diesel   | 53.60%                   | Available                  | Available                   | Already well established in the market                 | 0.0698                           |
| Methanol | 51.86%                   | Available                  | Available                   | Increase of range in the next years                    | 0.0102 – 0.01425                 |
| Ammonia  | 38.75%                   | Not Available              | Not Available               | First samples available in 2024-2026                   | -                                |
| Hydrogen | No information was found | Not Available              | Available (Dual fuel)       | Increase of range and availability of models from 2024 | -                                |

## 5. FUEL CELLS

Fuel cells convert chemical energy of a compound into electrical one and compared with other direct electricity production systems such as photovoltaic panels, this technology offers higher power capacity and better efficiency performances[94]. Therefore, thanks to the hydrogen's high energy density and high power supply availability, makes this technology one of the most promising energy generation solutions for heavy-duty vehicles[95].

The main difference with respect to batteries is that fuel cells can produce electricity as long as the fuel is supplied. Therefore, it can work continuously while a battery lasts for a limited period of time and after running out of energy needs to be recharged again which usually takes a considerable amount of time[96].

A fuel cell is a layered combination of two electrodes, one in each side, and an electrolyte which produces electricity through some electrochemical reactions. For the case of a PEMFC hydrogen molecules react with the catalyst producing protons (H<sup>+</sup>) and electrons (e<sup>-</sup>). Then, thanks to a membrane that is permeable only for positive ions, protons cross this membrane to the other side of the fuel cell. For the electrons the path to follow is different as they go to the other side through a wire which is connected to both sides in the outside of the cell. Once positive and negative ions meet in the other side, they react with oxygen molecules and water is produced as a by-product[97][98].

Nowadays, there are many types of fuel cells, but the most developed ones are: Proton Exchange Membrane Fuel Cell (PEMFC), Direct Methanol Fuel Cell (DMFC), Phosphoric Acid Fuel Cell

(PAFC), Alkaline Fuel Cell (AFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC)[96].

PEMFC is the most developed fuel cell for transport applications because it gives the possibility to be integrated in a transportation system together with an on-board hydrogen generation system[99]. According to O. Z. Sharaf et al. [98] PEMFC's power supply ranges from 10 to 300 kW, while according to P. Sharma et al. [100] this power ranges from 1 W to 500 kW. Anyway, depending on the desired power these fuel cells may be connected in series and/or parallel and form a fuel cell stack[101]. Rivarolo et al. [102] considered two branches of 180 kW, each one made of six 30 kW fuel cell stacks. There was no more information found about higher powered fuel cells which limits the application range for heavy transport systems considerably.

According to Y. Wang et al. [99], PEMFC fuel cell's operating temperature ranges from 50°C to 100°C. Nevertheless, Bengt Sundén indicated that operating temperatures could start from 30°C[96] and, finally, Sharaf et al. put the highest temperature limit up to 180°C[98]. The contrasted efficiencies for the PEMFC didn't vary that much from some authors to others, and most of them concluded that the efficiency of this kind of fuel cell ranges from 40% to 60%[94][96][98][99][103].

Sørensen and Spazzafumo [104] suggested that hydrogen fuelled fuel cells used in transportation should not be started running with the fuel cell directly and batteries should be included to start with the cold running of the transport. Once the vehicle is running the battery can be powered again with the energy produced by the fuel cell, therefore, there's no need to recharge this battery. According to Sørensen and Spazzafumo, including a battery in a fuel cell running system improves its functionality.

As it has been mentioned before, this review not only aims to compare the efficiencies of the power systems, it also considers the occupied space of each of them, both fuel tanks and power generation systems. To obtain an approximate value of a PEMFC stack, it was considered the new vehicle released by Toyota, the Toyota Mirai 2022 which runs with a PEMFC supplied with compressed stored hydrogen[105]. Thanks to the technical specifications document provided by the company, for an output power of 128 kW and a stored energy of 187 kWh, the size of the fuel cell stack is of 142.2 L[106]. Therefore, an approximate power output/fuel cell stack size ratio is 0.9 kW/L and the fuel cell volume stored energy ratio is 0.76 L/kWh.

## **6. ONBOARD HYDROGEN GENERATION**

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In the last decade using hydrogen for mobility has gained interest in the transport sector[107], but most of the suggested applications are based on the transport and storage of the compressed or liquified hydrogen. Nevertheless, it has been seen that hydrogen transportation through carriers turns out to be the best option by now. Therefore, companies working on the task of onboard power generation are coming up with ideas to obtain hydrogen out of the carrier to make use of it through a fuel cell.

Element1Marine[108] together with Ardmore Shipping Corporation[109] and Maritime Partners[110] have developed an onboard hydrogen generation system [111] to produce hydrogen onsite, onboard and on-demand out of the reaction between methanol and water. This process is based on the steam methanol reforming process in which methanol reacts with water vapour and hydrogen, carbon dioxide and carbon monoxide are produced. Usually, this reaction takes place in a reactor and after that, in order to obtain hydrogen with a high level of purity, it is taken through a gas purification system to dispose of the undesired gases. The pressure swing adsorption (PSA) system is one of the most used gas separation systems to obtain hydrogen after a reforming process[112].

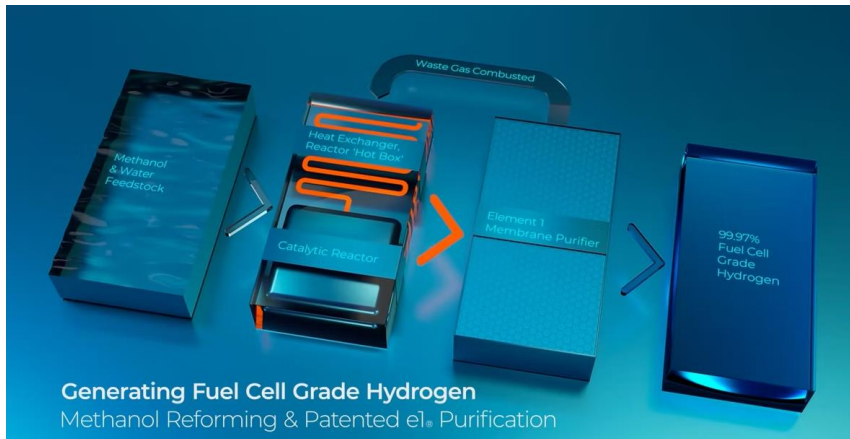


Figure 5 – e1Marine’s hydrogen production system [113]

IFPEN[114] together with Naval Group[115] also developed an onboard hydrogen generation system in 2015. In this case, it was carried out a project to develop a submarine that was powered by onboard generated hydrogen[116].



Figure 6 – The reformer



Figure 7 – The Water gas shifting unit

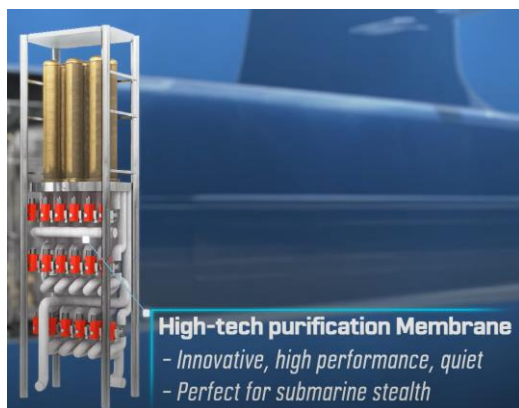


Figure 8 – The purification membrane

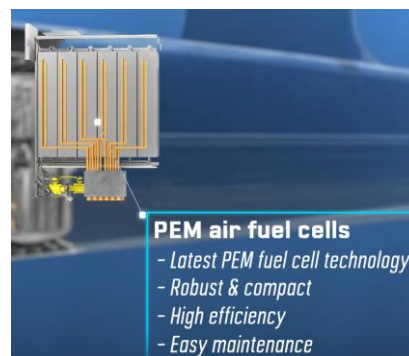


Figure 9 – The PEM FC



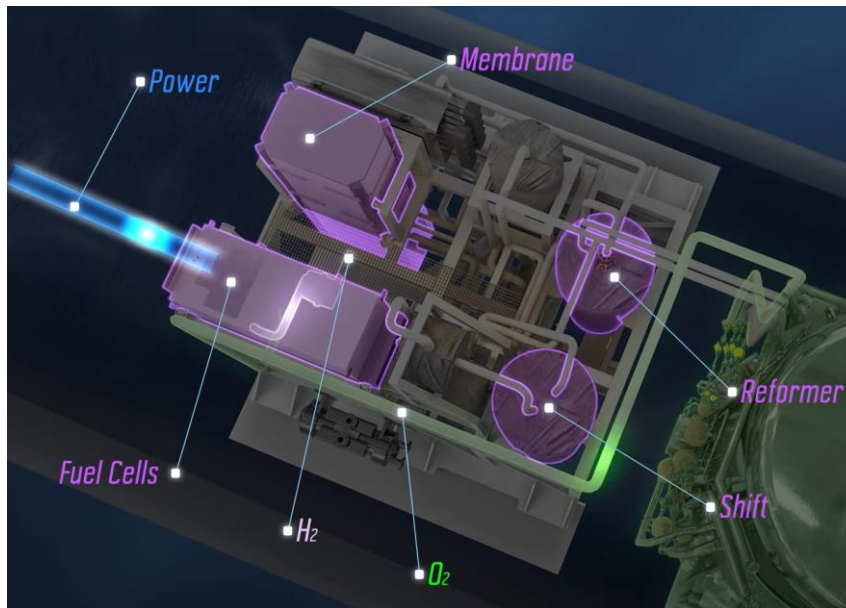


Figure 10 – The power System's scheme

To give an end to this section, it has to be mentioned that Navantia developed an air independent propulsion power system called S-80 Programme in 2020 that claims that has successfully achieved its air independence goal to avoid daily snorkelling operations. This submarine is powered with a fuel cell which is fuelled with hydrogen coming from the onboard processing of bioethanol and oxygen[117].

## 7. MEMBRANE REACTORS

Membrane reactor technology fall within the strategy of Process Intensification strategy that aims to improve and re-designe processes so that more compact and efficient systems are obtained. This allows for the better exploitation of raw materials and reduces plant volumes and energy consumptions[27].

In a membrane reactor, chemical reaction and separation occur simultaneously to obtain higher conversion rates at milder conditions. Membrane reactors have the advantage of obtaining higher reaction rates than thermodynamic conventional systems have[118]. This is due to the shifting of the equilibrium of the chemical reaction. As the produced hydrogen passes through the membrane, the hydrogen remaining in the retentate side decreases, therefore the reaction tends to increase its activity and more hydrogen is produced. As a result, more hydrogen is permeated.

Increasing the pressure difference between the permeate and retentate side (higher in the retentate side than in the permeate side) or introducing a sweep gas in the permeate side to reduce the partial pressure of the hydrogen results beneficial to obtain higher conversion rates[119][120]. Figure 11 shows the difference between membrane reactors and traditional reactors regarding their conversion rates. In the traditional processes firstly, the reaction happens in the reactor and secondly, the separation occurs thanks to a purification technology (membrane or any other), while a membrane reactor is able to achieve the same result or even a better one in just one step.

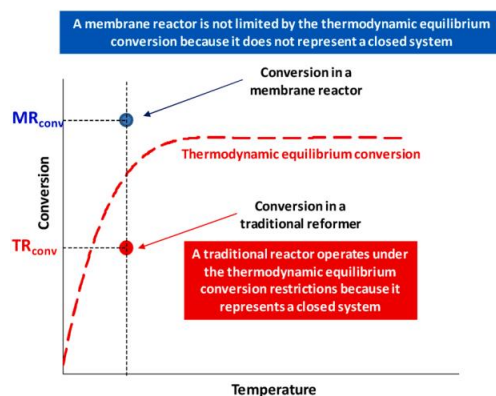


Figure 11 – Comparison between membrane reactors and traditional reactors [121]

There are three ways to classify this technology: (1) based on the type of catalyst configuration, (2) based on the type of membrane material or (3) based on the transport mechanism. The first classification criterion corresponds to the type and configuration of the catalyst used in the MR. The fixed-bed configuration is the main configuration[122] in which the catalyst is packed inside the reactor in an strategic position. In the tubular packed bed configuration, there are two ways to locate the catalyst: one is in the membrane tube (A) and the second in the shell side (B) as shown in Figure 12. To achieve a high production efficiency multi-tubular configurations are used[118].

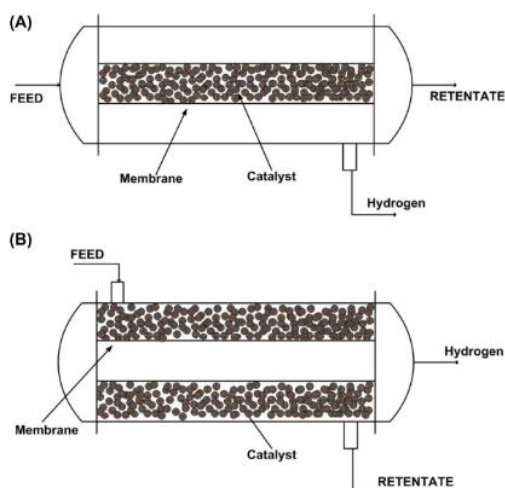


Figure 12 – Membrane reactor catalyst in the tube (a) and catalyst in the shell (B) configuration[118]

According to the second classification criterion, there are two types of membrane reactors: organic/polymeric and inorganic. On the one hand, organic membrane reactors are bioreactor membranes that are often used for removing pollutants from water or wastewater treatment. For these kind of membrane reactors, contamination of the membrane is the main challenge. On the other hand, within the inorganic membrane reactors, metallic membrane-based reactors are found where Palladium-based membrane reactors are the most studied ones.

Another aspect to consider about membrane reactors is the configuration of the reactor. There are two main configurations that are used for chemical reactions: fluidized bed membrane reactors and packed bed membrane reactors. In terms of required membrane area to obtain a desired hydrogen production fluidized bed membrane reactors have shown better performances due to a better control of temperature and mass transfer resistances. Packed bed membrane reactors need 20-25% more membrane area than fluidized ones[123].

Table 7 shows the most common hydrogen separation membranes and their characteristics. Its high H<sub>2</sub> selectivity (>10000) and H<sub>2</sub> flux makes palladium-based membranes one of the best choices to obtain pure hydrogen from a hydrogen carrier. Nevertheless, scientists are working on other membranes for hydrogen separation purposes.

Table 7 - Comparison of membrane types for hydrogen separation [124]

| Membrane type   | Polymeric                                 | Microporous ceramic                          | Porous carbon                        | Dense metallic                       | Proton conducting dense ceramic |
|---|---|--|--------------------------------------|--------------------------------------|---------------------------------|
| Materials   | Polymers                                  | Silica, alumina, zirconia, titania, zeolites | Carbon                               | Palladium alloys                     | Proton conducting ceramics      |
| Temperature (°C)  | <100                                      | 200-600                                      | 500-900                              | 300-600                              | 600-900                         |
| H <sub>2</sub> flux (10 <sup>-3</sup> mol m <sup>-2</sup> s <sup>-1</sup> ) at Δp=1 bar | Low                                       | 60-300                                       | 10-200                               | 60-1000                              | Jun-80                          |
| H <sub>2</sub> selectivity  | Low                                       | 5-139  | Apr-20                               | >1000                                | >1000                           |
| Transport mechanism   | Solution-diffusion                        | Molecular sieving                            | Surface diffusion, molecular sieving | Solution-diffusion                   | Solution-diffusion              |
| Stability issues  | Swelling, compaction, mechanical strength | Stability in H <sub>2</sub> O                | Brittle, oxidation                   | Phase transition at low T and high P | Stability in CO <sub>2</sub>    |
| Poisoning issues  | HCl, SO <sub>x</sub> , CO <sub>2</sub>    | -  | Strong adsorbing vapours, organics   | H <sub>2</sub> S, CO                 | H <sub>2</sub> S                |
| Cost  | Low                                       | Low  | Low                                  | Moderate                             | Low                             |

According to most of the authors and their conclusions, it is determined that the most effective and also the most used membrane reactor for both processes is palladium-based membrane reactor[125][126][127][128]. Nevertheless, other kind of membrane reactors are being studied as well, carbon molecular sieve membranes[129] or proton conducting ceramics [130][131] are two of those. Not only the membrane material used is important, but also other characteristics such as temperature, pressure or type of catalyst will determine the efficiency of the system.

## 7.1. PALLADIUM BASED MEMBRANE REACTORS

Palladium is a rare and silvery-white metal that has numerous applications because of its properties, and in addition, lately, it has been one of the key metals in hydrogen technologies. Hydrogen easily diffuses through heated palladium, enabling Pd-based membrane reactors to obtain high purity hydrogen[132].

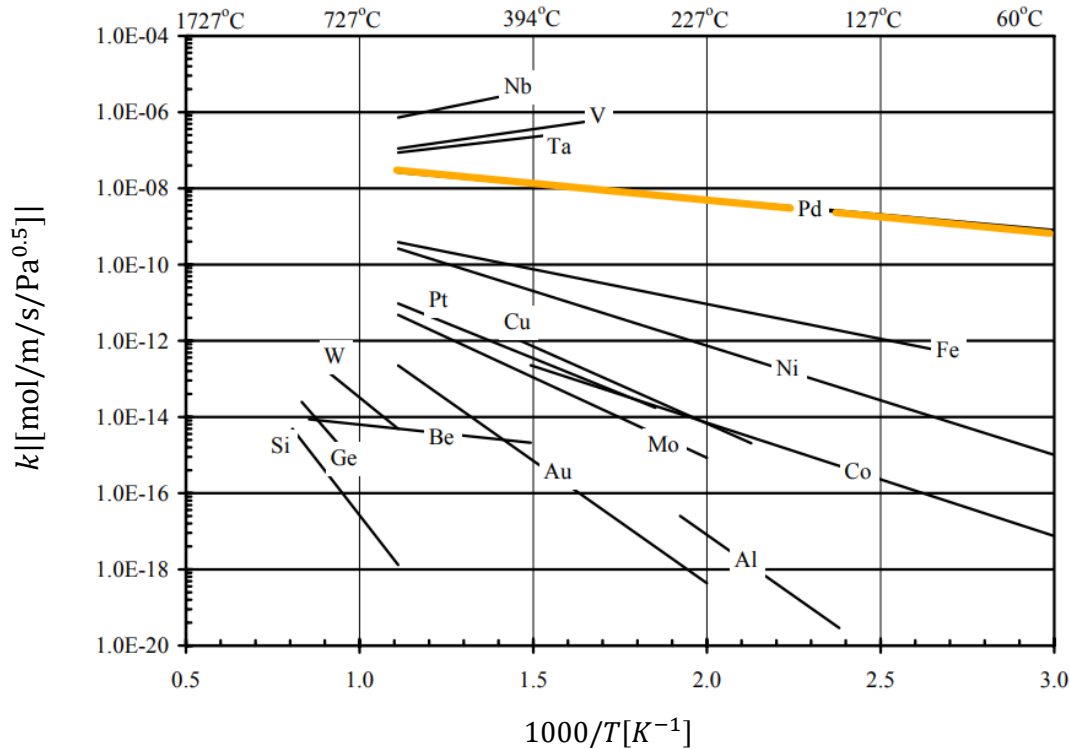


Figure 13 - Permeability of various pure materials[133]

Palladium based membranes are mainly used for hydrogen separation and purification processes. Its high permeability makes this material highly suitable for this kind of separation processes as it can be seen in Figure 13. However, hydrogen embrittles palladium at low temperatures; therefore, usually palladium is found alloyed to other materials such as Ag, Ni or Au which help improving the stability of the membrane[124][134]. In addition, Habib et al.[135] showed in their review how the permeation of the membrane improves as palladium is alloyed with other materials. Table 8 show the Pd-alloyed Pd permeation ratio from Habib et al's review.

Table 8 - Enhanced Hydrogen Permeability of Pd Alloys as Compared to Pure Pd[135]

| Pd-alloy | wt % of alloy metal | Permeation ratio Pd-alloy/Pd |
|----------|---------------------|------------------------------|
| Pd       | 0                   | 1                            |
| Pd-Ag    | 23                  | 1.7                          |
| Pd-Y     | 6.6                 | 3.5                          |
| Pd-Y     | 10                  | 3.8                          |
| Pd-Ce    | 7.7                 | 1.6                          |
| Pd-Au    | 5                   | 1.1                          |
| Pd-Cu    | 10                  | 0.48                         |
| Pd-Ru-In | 0.5, 6              | 2.8                          |
| Pd-Ag-Ru | 30, 2               | 2                            |
| Pd-Ag-Ru | 19, 1               | 2.6                          |

Not only the used material has an influence on the permeation of hydrogen but also depends on temperature and the presence of CO, which may reduce this performance as well. In fact, CO molecules react with palladium decreasing the hydrogen dissociation sites and thus reducing the adsorption[124].

In the last decade, thinner Pd-based membranes have been produced. Two reasons are behind this strategy. One is the high cost of the material (61.05 €/gr for Pd[136]). The other one is the permeation of the membrane, the thinner the membrane is the higher the permeation becomes. On the contrary, very thin selective layers face some problems that must be considered. From one side, very thin Pd layers have enough mechanical stability to withstand transmembrane pressures.

To face this mechanical instability, these thin films are deposited onto a porous support so that they meet the necessary mechanical characteristics[137]. On the other side, concentration polarization is enhanced by very permeable membranes strongly affecting the performance of the separation process because it reduces the selectivity of separation and the membrane's lifetime[138]. To reduce this concentration polarization, flow rates are increased and spacers to promote turbulence are included.

Each membrane reactor can have a different number of membranes, Tecnalia[139] scaled up for BIONICO project (2015-2018)[140][141] a 100 membranes-built prototype, each one of 40 cm in length[137]. A membrane reactor is mainly conformed by three sections:

- The feed section consists of a feed gas supply from cylinders and mass flow controllers to achieve the desired flow and composition rates at the inlet.
- The membrane module section consists of a stainless-steel reactor, commonly build up with electric ovens and pressure transmitters to obtain the desired temperature and pressure and the top and bottom of the reactor.
- The analysis section consists of two inline extractive gas analysers. On the retentate side, the analyser is calibrated for CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> and on the permeate side is calibrated for H<sub>2</sub> and CO.

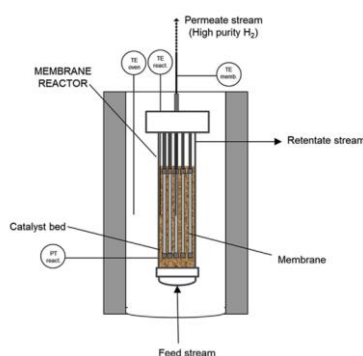


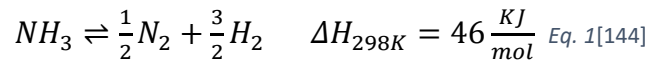
Figure 14 – Membrane reactor scheme[137]

Several studies have stated that palladium based membranes have efficient results concerning dehydrogenation and hydrogen purification[137][126][118]. Apart from alloying it with other metals[134], ceramic recovery can also enlarge this membrane's lifespan[142]. In addition, Table 8 shows the enhancement of the membrane's permeability when this is alloyed compared to a pure Pd based membrane.

### 7.1.1. MEMBRANE REACTOR FOR LIQUID AMMONIA DECOMPOSITION PROCESS

Liquid ammonia is one of the proposed alternatives for storing hydrogen. F.Galucci et al. [118] have shown that the decomposition of ammonia to hydrogen through membrane reactors has highly efficient results at lower temperatures than conventional systems. Palladium membrane reactor in addition to ruthenium based catalyst is one of the most successful membrane reactor-catalyst combinations for ammonia decomposition[126].

Using liquid ammonia as a hydrogen carrier has many benefits for the challenge of storing and transportation, but also for the challenge of reducing carbon emissions[143]. Ammonia is a compound which is formed by hydrogen and nitrogen atoms and is widely used in the industrial sector.



As hydrogen separates from nitrogen in an endothermic reaction, H<sub>2</sub> and N<sub>2</sub> molecules are produced. Nitrogen molecules are harmless and odourless molecules and confirm 78% of the air[145]. Conversion rates up to 98% are possible at temperatures as low as 425°C[146]. After conversion hydrogen is stored or used in a fuel cell while nitrogen is released to the atmosphere without producing any harm to the atmosphere.

On the whole, an advantage for this carrier is that manipulation of liquid ammonia is not something new as it is well established in the industrial sector. Liquid ammonia shipping and tube transportation is done in a daily basis[143][147]

After publications review in which hydrogen generation through membrane reactors were analysed, a table was built to gather information about the details for each study. In this case, Table 9 shows which were the parameters to produce hydrogen from ammonia.

Cechetto et al. [125] proved that increasing the thickness of the membrane ultra-pure hydrogen production can be achieved. What's more, for a membrane whose thickness is over 6 µm ultra-pure hydrogen is produced at pressures below 5 bar. The downside is that the thicker is the selective layer the less hydrogen permeates through it. Therefore, an equilibrium must be found between the permeability which needs to be high enough to recover as much produced hydrogen as possible, but at the same time must be selective enough to avoid impurities in the permeate side. If this hydrogen is going to be destined to be used in fuel cells purity must meet the quality of a fuel cell application.

In this case, at high temperatures such as 500°C high conversion rates are achieved and pressure variations do not affect this result. Whereas it does significantly vary the hydrogen recovery which increases and slightly the purity which decreases as pressure increases. On the other side, temperature variation affects the conversion of the ammonia and recovery which are higher as well. Purity remains constant at this variation.

An important point to take from this study is that it was decided to take advantage of the retentate stream and use it via combustion to supply the required heat to the reactor and improve the overall performance of the device.

Cechetto et al. [126] demonstrated that full NH<sub>3</sub> decomposition was possible at temperatures above 425°C as well as 86% of hydrogen recovery and 99.98% of purity in the permeate stream. What's more, vacuum was applied in the permeate side and it was proved that thanks to this technique higher recovery rates and N<sub>2</sub> conversions were achievable.

As it can be seen in Table 9, most of the reviewed articles are based on Ruthenium based catalyst.

Zhang et al. [148] compared the influence that has the designed configuration for the reactor. It is proved that the tube-wall reactor has better performances with less catalyst than comparing it with the packed bed one with more catalyst. At the same time, it is shown that better conversion rates are achieved with thinner membranes. Reducing the thickness of the membrane enables to obtain high performances without needing high temperatures which is favourable for the lifespan of the membrane reactor.

High pressures such as 10 bars have shown that the hydrogen yield didn't vary with the change in temperature or ammonia feed flow according to Itoh et al.'s study [149]. Indeed, high conversion rates and permeation without heating supply were achieved in the study. This review considers the palladium-based membrane with Ruthenium filled catalyst one of the best devices to produce in situ hydrogen.

Apart from the mentioned operative conditions and parameters, the consequences that have the variation of the feed flow rate is also studied in the articles. In general, high conversion rates as well as high purity rates are achieved in the checked reviews which indicates that membrane reactor technologies are effective when decomposing ammonia to obtain pure hydrogen.

For the case of the ammonia, few of the studies used sweep gas. Indeed, even if the conversion and recovery rates increase with the application of a sweep gas in the permeate side, it can't be ignored that afterwards this sweep gas must be removed as well if the correct performance of the fuel cell is desired which increases the energy consumption of the process.

One of the main drawbacks of this hydrogen carrier is its toxicity. As it was mentioned before, there are further possibilities to store hydrogen and solid tablets such as metal ammine chlorides offer high hydrogen density concentrations. They are considered an interesting ammonia storage system and, hence, a hydrogen indirect storage system[150].  $\text{NH}_3$  molecules are released with the increase of temperature via desorption process. This technology solves the toxicity risk problem of storing ammonia. The risk of explosion is a fact to consider too, and flammability and explosion limits must be taken into account when taking advantage of this carrier[151].

The required space to store this carrier was calculated out of the energy demand of the vessel were the ratio for the tank volume/stored carrier volume was included. This ratio was obtained from Snyder Industries Inc. [152] which resulted to be around 1.4 and 1.46. The bigger the amount of stored ammonia, the smaller the ratio.

Table 9 - Membrane reactors for hydrogen generation from ammonia decomposition. <sup>3</sup>

| Membrane reactors                         | Catalyst                          | Membrane thickness $\mu\text{m}$ | Carrier conversion [%] | H <sub>2</sub> Recovery [%] | H <sub>2</sub> Permeate purity [%] | Membrane area [cm <sup>2</sup> ] <sup>4</sup> | Membrane reactor volume [cm <sup>3</sup> ] | Catalyst weight [g] | WHSV [h <sup>-1</sup> ] | Feed flow rate [mol/s] <sup>4</sup> | Load-to-surface ratio [mol/s cm <sup>2</sup> ] | Reaction Temperature [°C] | Reaction Pressure [bar] | Sweep gas flow rate mol/s | Sweep ratio | Sweep gas      | Permeate side pressure [bar] | Source |
|---|-----------------------------------|----------------------------------|------------------------|-----------------------------|------------------------------------|---|--|---------------------|-------------------------|-------------------------------------|--|---------------------------|-------------------------|---------------------------|-------------|----------------|------------------------------|--------|
| Thin Pd-Ag/Al <sub>2</sub> O <sub>3</sub> | Ru                                | 6                                | 99.8                   | 88.9                        | 99.99                              | 395.84  | 445.32                                     | 250.00              | -                       | 4.17E-01                            | 1.05E-03                                       | 500                       | 5                       | -                         | -           | -              | 1                            | [125]  |
| Pd-Ag                                     | Ru                                | 4.61                             | 99.998                 | 86                          | 99.998                             | 395.84  | 445.32                                     | 250.00              | -                       | 4.17E-01                            | 1.05E-03                                       | 450                       | 4.5                     | -                         | -           | N.S.P          | 1                            | [126]  |
| Silica                                    | Al <sub>2</sub> O <sub>3</sub>    | -                                | 95                     | -                           | -                                  | 25.13   | 7.85                                       | 0.05                | -                       | 7.44E-05                            | 2.96E-06                                       | 450                       | 1                       | 7.44E-05                  | -           | N <sub>2</sub> | 0.05                         | [153]  |
| Pd/PSS                                    | Ru-carbon                         | 40                               | 98.1                   | -                           | -                                  | 17.30   | -  | 0.30                | -                       | 6.68E-02                            | 3.86E-03                                       | 362                       | -                       | 2.23E-04                  | -           | He             | 1                            | [154]  |
| Pd-Ag                                     | -                                 | 6                                | 99.5                   | -                           | -                                  | 34.30   | -  | -                   | -                       | -                                   | -  | 670                       | 36                      | 2.23E-03                  | 0.857       | -              | 1                            | [155]  |
| Pd  | Ru (CMR)                          | 6                                | 98                     | 87.5                        | 99.7                               | -   | -  | -                   | -                       | 4.16E-05                            | -  | 400                       | 5                       | -                         | -           | N.S.P          | 1                            | [148]  |
| Pd  | Ru (PBMR)                         | 6                                | 98                     | 66                          | 99.2                               | -   | -  | -                   | -                       | 1.02E-04                            | -  | 520                       | 3                       | -                         | -           | N.S.P          | 1                            | [148]  |
| Pd  | Ni/Al <sub>2</sub> O <sub>3</sub> | -                                | 99.93                  | -                           | 99.999                             | 94.25   | 30.00                                      | -                   | -                       | 1.66E-04                            | 1.76E-06                                       | 550                       | 10                      | -                         | -           | N.S.P          | 1                            | [156]  |
| Pd-Ag/Al <sub>2</sub> O <sub>3</sub>      | Ru                                | 2                                | 99.99                  | -                           | -                                  | 8.48  | 6.36                                       | -                   | -                       | 6.79E-04                            | 8.01E-05                                       | 375                       | 10                      | -                         | -           | N.S.P          | 0.06                         | [149]  |
| Pd  | Ru                                | -                                | 99.4                   | -                           | 99.999                             | -   | -  | -                   | -                       | -                                   | -  | 400                       | 5                       | -                         | -           | N.S.P          | 1                            | [157]  |

<sup>3</sup> N.S.P: No Sweep Gas

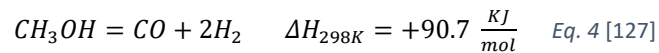
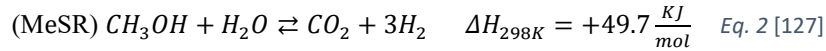
<sup>4</sup> Used equations are shown in the appendix



## 7.1.2. MEMBRANE REACTOR FOR METHANOL STEAM REFORMING PROCESS

Scientists are tackling the problem of carbon dioxide and carbon monoxide emissions to the atmosphere. GHG are released during the process of obtaining hydrogen from a hydrocarbon[158]. This process is known as steam reforming process and it's the reaction between hydrocarbons and water vapour. Natural gas is usually the principal hydrocarbon from which hydrogen is obtained, but this process can be also used with other hydrocarbons as well.

An advantage of methanol is that it doesn't have any C-C bond which consequently requires low reforming temperatures (513 K - 533K). The main reaction taking place in the methanol steam reforming (MeSR) process is endothermic(MeSR)  $CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2$   $\Delta H_{298K} = +49.7 \frac{KJ}{mol}$  Eq. 2[158]. It is important to understand that in the methanol steam reforming process, other reactions take place as well. These reactions are the water gas shifting (WGS) reaction (WGS)  $CO + H_2O = CO_2 + H_2$   $\Delta H_{298K} = -41.2 \frac{KJ}{mol}$  Eq. 3 and the methanol decomposition reaction  $CH_3OH = CO + 2H_2$   $\Delta H_{298K} = +90.7 \frac{KJ}{mol}$  Eq. 4. In the methanol decomposition reaction carbon monoxide is produced as a by-product which leads to poisoning problems[159].



Water vapour reacts with the hydrocarbon and hydrogen and carbon dioxide and monoxide are produced. Because of these emissions, if methanol is going to be proposed as a carrier of H<sub>2</sub> for onboard power generation, a carbon capture system must be integrated.

This hydrogen carrier needs to be supplied with water in order to obtain hydrogen from it. Therefore, two options are identified, either having a fuel tank full of water-methanol mixture either having two separate tanks one for water and the other for methanol. D.Palo et al. [160] determined that the water supply for the steam reforming of methanol was 1.125 kg H<sub>2</sub>O/kg methanol. Thanks to this data it is going to be calculated the total demand for water supply for this process and its tank's volume occupancy. The ratio between tank volume and stored water is obtained from General Industries Inc. [161] in which the ratio was 1.4364 m<sup>3</sup> tank/water [162] and 1.3119 m<sup>3</sup> tank/water [163] where the ratio got smaller the bigger was the amount of water that was stored.

In the case of methanol scientific literature review was done as well. Different articles were analysed and information was collected the same way it was done for the ammonia. Table 10 shows the data for each membrane reactor with their corresponding operating parameters.

All of the membrane reactors were based on Palladium. All the presented Pd based membranes were alloyed with another component because it was demonstrated that reduces the embrittlement of the membrane and obtains higher methanol conversion rates and hydrogen recovery rates [79]. The membrane reactors shown in the table are palladium alloyed with silver. The common configuration for this kind of membrane is the following one: a thin Pd layer rest over a thicker layer of a porous material, for example, alumina (Al<sub>2</sub>O<sub>3</sub>) [164][128] or porous stainless steel (PSS) [165] [84]; but other configurations such as dense Pd-Ag membranes have been studied as well [128].

F. Gallucci and A. Basile [166] concluded that the reaction temperature, the reaction pressure and the sweep gas flow rate have positive consequences on the results. Indeed, the higher is the sweep

gas flow rate the higher is going to be the hydrogen recovery. What's more, the higher are the reaction temperature and pressure, the higher is the conversion rate. Hence, increasing these operating conditions improves the performance of the membrane reactor[166]. But raising the reaction pressure could have downsides as well, for instance, hydrogen purity in the outlet can decrease due to the increase of the driving force that could lead to undesired components permeate through the membrane to the permeate side[167].

Therefore, as a possible solution to this situation, it was studied if decreasing the partial pressure of the permeate species would result in having high conversion rates and COx free hydrogen recovery rates without decreasing the purity in the outlet[120]. The partial pressure of a gas is the pressure that this gas would have if it was the only gas of the mixture occupying that same space. There are two ways to reduce the partial pressure of a gas in a gas mixture, one of the ways is reducing the pressure of the permeate side producing vacuum and the other is introducing a sweep gas on the permeate side[168]. As carbon monoxide damages the fuel cell, it is important to ensure that no carbon monoxide crosses the membrane or permeates as little as possible[169].

The sweep gas is a gas that is inserted in the permeate side of the membrane reactor with the purpose of reducing the partial pressure of the substance that is desired to be permeated. The upside of the sweep gas is that high hydrogen recovery rates are achieved as well as hydrogen purity. Nevertheless, the downside is that this sweep gas must be removed with another device if the obtained hydrogen is going to be used in applications that require really high purity such as fuel cells[170]. This obstacle can be faced if steam is used as sweep gas. Another point to take into account about sweep gas is that it has been proved that up to one point of sweep ratio the difference in the results is minimum[120] [86].

Regarding the catalyst, most of the studies done for obtaining pure hydrogen from steam methanol reforming process used copper-based catalyst. It can be seen in the table that most of them were copper-oxides combined with zinc-oxides and alumina oxides. Depending on the activity of the catalyst, the reactions were carried out at different temperatures and pressures. One of the studies shows that for different used catalyst at the same operating conditions, different results were obtained[127]. But not only copper is used as catalyst, Ruthenium-based catalyst are shown as well. It was proved that higher temperatures were possible for this material-based catalyst than for Cu-based ones, which, as a result had higher conversion rates than this last one. Therefore, high temperatures and low pressures were used for the case in which Ruthenium was used as a catalyst, while lower temperatures and higher pressures were used for the Copper-based ones[128]. Increasing the alumina was also seen to be beneficial to obtain higher activity at the catalyst without the need for increasing temperatures[171].

The equations used in the articles reviewed to complete this table are the following ones:

$$CH_3OH \text{ conversion } (X_{Cl_3OH}, \%) = \frac{CH_3OH_{in} - CH_3OH_{out}}{CH_3OH_{in}} \cdot 100 \text{ Eq. 5 [164]}$$

$$H_2 \text{ recovery, (H.R., \%)} = \frac{H_2 \text{ permeate}}{H_2 \text{ permeate} + H_2 \text{ retentate}} \cdot 100 \text{ Eq. 6 [171]}$$

$$\text{Weight Hourly Space Velocity (WHSV, h}^{-1}\text{)} = \frac{CH_3OH_{IN}}{m_{catalyst}} \text{ Eq. 7 [171]}$$

$$\text{Sweep Gas Ratio (SGR)} = \frac{N_2 \text{ molar flow rate in the permeate side}}{CH_3OH_{in} \text{ molar flow rate}} \text{ Eq. 8 [120]}$$

Table 10 - Membrane reactors for hydrogen generation out of methanol. \* These numbers were calculated in order to obtain the desired units.F.C.Q: Fuel Cell Quality

| Membrane reactors   | Catalyst                                       | Membrane thickness $\mu\text{m}$ | Carrier conversion [%] | H <sub>2</sub> Recovery [%] | H <sub>2</sub> Permeate purity [%] | Membrane active area $\text{cm}^2$ <sup>5</sup> | Membrane volume $\text{cm}^3$ | Catalyst weight [g] | WHSV <sup>6</sup> [ $\text{h}^{-1}$ ] | Feed flow rate [ $\text{mol/s}$ ] <sup>5</sup> | Load-to-surface ratio [ $\text{mol/s cm}^2$ ] <sup>5</sup> | Feed ratio [mol H <sub>2</sub> O /mol CH <sub>3</sub> OH] | Reaction Temperature [ $^{\circ}\text{C}$ ] | Reaction Pressure [bar] | Sweep gas flow rate mol/s | Sweep ratio [sweep gas mol/H <sup>2</sup> mol] | Sweep gas      | Permeate side pressure [bar] | Source |
|---|--|----------------------------------|------------------------|-----------------------------|------------------------------------|---|-------------------------------|---------------------|---------------------------------------|--|--|---|---|-------------------------|---------------------------|--|----------------|------------------------------|--------|
| Dense Pd-Ag   | D.S  | 20                               | 98.331                 | 94.276                      | F.C.Q                              | 62.83   | 78.54                         | -                   | -                                     | -  | -  | 3.00  | 588   | 8                       | -                         | 4  | -              | -                            | [166]  |
| (Thin Pd)/Al <sub>2</sub> O <sub>3</sub>                      | CuO/ZnO /Al <sub>2</sub> O <sub>3</sub>        | 8                                | 90.1                   | 63                          | -                                  | 20.42   | 21.21                         | 0.20                | 2.73                                  | 4.74E-06                                       | 2.32E-07   | -   | 300   | -                       | -                         | -  | -              | 1                            |        |
| (Thin Pd)/Al <sub>2</sub> O <sub>3</sub>                      | CuO/ZnO  | 8                                | -                      | 57                          | 90                                 | 20.42   | 21.21                         | 0.20                | 2.73                                  | 4.74E-06                                       | 2.32E-07   | 1.50  | 330   | 1.5                     | -                         | -  | -              | 1                            |        |
| (Thin Pd)/Al <sub>2</sub> O <sub>3</sub>                      | CuO/ZnO  | 8                                | -                      | 62                          | 90                                 | 20.42   | 21.21                         | 0.20                | 2.73                                  | 4.74E-06                                       | 2.32E-07   | 1.50  | 330   | 2                       | -                         | -  | -              | 1                            |        |
| (Thin Pd)/Al <sub>2</sub> O <sub>3</sub>                      | CuO/ZnO  | 8                                | -                      | 64                          | 88                                 | 20.42   | 21.21                         | 0.20                | 2.73                                  | 4.74E-06                                       | 2.32E-07   | 1.50  | 330   | 2.5                     | -                         | -  | -              | 1                            | [167]  |
| (Thin Pd)/Al <sub>2</sub> O <sub>3</sub>                      | CuO/ZnO  | 8                                | 12.4                   | -                           | -                                  | 20.42   | 21.21                         | 0.20                | 0.95                                  | 1.65E-06                                       | 8.08E-08   | 2.50  | 220   | 1                       | -                         | -  | -              | 1                            |        |
| (Thin Pd)/Al <sub>2</sub> O <sub>3</sub>                      | CuO/ZnO  | 8                                | 47.1                   | -                           | -                                  | 20.42   | 21.21                         | 0.20                | 0.95                                  | 1.65E-06                                       | 8.08E-08   | 2.50  | 260   | 1                       | -                         | -  | -              | 1                            |        |
| (Thin Pd)/Al <sub>2</sub> O <sub>3</sub>                      | CuO/ZnO  | 8                                | 97.4                   | -                           | -                                  | 20.42   | 21.21                         | 0.20                | 0.95                                  | 1.65E-06                                       | 8.08E-08   | 2.50  | 300   | 1                       | -                         | -  | -              | 1                            |        |
| Dense Pd-Ag   | CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>         | 50                               | 42.5                   | 47.8                        | -                                  | 15.71   | 87.96                         | -                   | -                                     | -  | -  | 1.00  | 220   | 2                       | -                         | 2  | N <sub>2</sub> | -                            |        |
| Dense Pd-Ag   | CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>         | 50                               | 46*                    | 59*                         | -                                  | 15.71   | 87.96                         | -                   | -                                     | -  | -  | 1.00  | 220   | 2                       | -                         | 6  | N <sub>2</sub> | -                            | [120]  |
| Dense Pd-Ag   | CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>         | 50                               | 47.4                   | 60.2                        | -                                  | 15.71   | 87.96                         | -                   | -                                     | -  | -  | 1.00  | 220   | 2                       | -                         | 10   | N <sub>2</sub> | -                            |        |
| Dense Pd-Ag   | CuO/ZnO /Al <sub>2</sub> O <sub>3</sub>        | 50                               | 76.1*                  | -                           | F.C.Q                              | 48.07   | 87.96                         | 7.50                | -                                     | -  | -  | 2.43  | 250   | 1.25                    | 1.38E-05                  | -  | N <sub>2</sub> | 1                            | [172]  |
| Dense Pd-Ag   | CuO/ZnO /Al <sub>2</sub> O <sub>3</sub>        | 50                               | 67                     | -                           | F.C.Q                              | 48.07   | 87.96                         | 7.50                | -                                     | -  | -  | 2.43  | 250   | 1.25                    | 2.17E-04                  | -  | N <sub>2</sub> | 1                            |        |
| Dense Pd-Ag   | D.S  | 50                               | 100                    | 95                          | -                                  | -   | 87.96                         | -                   | -                                     | -  | -  | -   | 255   | 2                       | 2.20E-03                  | -  | N <sub>3</sub> | -                            |        |
| Dense Pd-Ag   | CuO/Al <sub>2</sub> O <sub>3</sub> /ZnO/MgO    | 50                               | 100                    | 15                          | F.C.Q                              | 47.12   | 87.96                         | 3.00                | -                                     | -  | -  | 4.50  | 450   | 1.3                     | 2.67E-04                  | -  | N <sub>2</sub> | 1                            |        |
| Dense Pd-Ag   | CuO/Al <sub>2</sub> O <sub>3</sub> /ZnO/MgO    | 50                               | 100                    | 40                          | F.C.Q                              | 47.12   | 87.96                         | 3.00                | -                                     | -  | -  | 4.50  | 450   | 1.3                     | 5.30E-04                  | -  | N <sub>2</sub> | 1                            | [127]  |
| Dense Pd-Ag   | CuO/Al <sub>2</sub> O <sub>3</sub> /ZnO/MgO 3g | 50                               | 52                     | -                           | -                                  | 47.12   | 87.96                         | 3.00                | -                                     | -  | -  | 3.00  | 250   | 1.3                     | 2.30E-04                  | -  | N <sub>2</sub> | 1                            |        |
| Dense Pd-Ag   | CuO/ZnO/Al <sub>2</sub> O <sub>3</sub> 7.5 g   | 50                               | 67                     | -                           | -                                  | 47.12   | 87.96                         | 7.50                | -                                     | -  | -  | 3.00  | 250   | 1.25                    | 2.17E-04                  | -  | N <sub>2</sub> | 1                            |        |
| Dense Pd-Ag   | CuO/ZnO/ Al <sub>2</sub> O <sub>3</sub>        | 3.9                              | 100                    | -                           | ~100                               | -   | 109.67                        | -                   | -                                     | -  | -  | 1   | 250   | 10                      | -                         | -  | N.S.G          | 1                            | [170]  |
| (Thin Pd)/PSS   | CuO/ZnO /Al <sub>2</sub> O <sub>4</sub>        | 20                               | 95                     | 97                          | F.C.Q                              | 60  | 19.00                         | -                   | 1.00                                  | -  | 1.39E-06   | 1.2   | 350   | 12                      | -                         | 1.2  | -              | <1                           | [173]  |
| (Thin Pd-Ag)/TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> | Ru-Al <sub>2</sub> O <sub>3</sub>              | -                                | 95                     | -                           | F.C.Q                              | 175.93  | -                             | -                   | -                                     | 1.28E-04                                       | 7.26E-07   | -   | 550   | 1.3                     | -                         | -  | -              | 1                            | [128]  |
| Dense Pd-Ag   | RuAl <sub>2</sub> O <sub>3</sub>               | 50                               | 100                    | 40                          | -                                  | 47.12   | -                             | -                   | -                                     | 1.28E-04                                       | 2.71E-06   | -   | 450   | 1.3                     | 5.27E-04                  | -  | N <sub>2</sub> | 1                            |        |
| Dense Pd-Ag   | CuO/Al <sub>2</sub> O <sub>3</sub> /ZnO/MgO    | 50                               | -                      | 93                          | F.C.Q                              | 45.55   | -                             | 4.00                | 0.36                                  | 1.25E-05                                       | 2.74E-07   | -   | 300   | 3                       | 9.50E-05                  | 3  | Steam          | 1                            | [171]  |
| Thin Pd/PSS   | Cu based                                       | 20-25                            | 99                     | -                           | F.C.Q                              | 70  | -                             | -                   | 1.3                                   | -  | -  | -   | 350   | 6                       | -                         | -  | -              | 1                            | [165]  |
| (Thin Pd)/Al <sub>2</sub> O <sub>3</sub>                      | CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>         | 7                                | 85                     | >40                         | F.C.Q                              | 17.0  | -                             | -                   | -                                     | -  | -  | -   | 330   | 2.5                     | 2.16E-05                  | -  | N <sub>2</sub> | -                            | [164]  |

<sup>5</sup> Used equations are shown in the appendix

<sup>6</sup> Weight Hourly Space Velocity

## 7.2. PROTON CONDUCTING CERAMICS

Proton conducting ceramic (PCC) membrane reactors offer the chance of obtaining pure hydrogen through reaction and separation at one step[174]. There are mainly three types of PCC membrane reactors: perovskites, polyphosphate composite and pyrochlore. Table 11 shows the perovskite-based materials for hydrogen separation and their hydrogen flux. Temperature ranges are higher compared to palladium based reactors, which in turn it improves the permeation of the hydrogen through the membrane[175].

Their feature to work at low temperatures thanks to high efficiencies, performance and stability makes these membranes an interesting opportunity to obtain pure hydrogen. Proton conducting ceramic membranes are able to obtain hydrogen at low temperatures that range between 25°C and 400°C[130].

This type of membrane reactor is destined to be used in electrolysis process among others with the purpose of obtaining pure hydrogen from steam[130][131]. Nevertheless, studies have shown that PCCs could work for any hydrogen containing gas[176]. On the whole, this technology is still in its developing phase and far from future applications but could have great importance in fields like nuclear fusion reactor engineering where scientist are looking for the best way of hydrogen separation under strong irradiation at high temperatures[177].

Table 11 -Perovskite-based materials for hydrogen separation [178]

| Material           | Membrane thickness (mm) | H <sub>2</sub> flux (ml cm <sup>-2</sup> min <sup>-1</sup> ) | T (°C) | Reference                  |
|--------------------|-------------------------|--|--------|----------------------------|
| SrCe0.95Tm0.05O3   | 0.15                    | 0.126  | 900    | Cheng et al. (2005)        |
| SrCe0.95Tm0.05O3-δ | 1.6                     | 0.039  | 900    | Qi and Lin (2000)          |
|                    | 3                       | 0.028  | 900    |                            |
| SrCe0.95Yb0.05O3-δ | 1.6                     | 0.023  | 900    | Qi and Lin(2000)           |
|                    |                         |  |        | Hamakawa et al. (1998)     |
| SrCe0.95Y0.05O3-δ  | 1.6                     | 0.028 (extrapolated)   | 900    | Qi and Lin (2000)          |
|                    |                         |  |        | Guan et al. (1998)         |
| SrCe0.8Y0.2O3-δ    | 1.6                     | 0.048  | 900    | Qi and lin (2000)          |
|                    |                         |  |        | Balachandran et al. (1998) |

## 7.3. CARBON MOLECULAR SIEVE MEMBRANES

Carbon molecular sieve membranes are inorganic membranes that offer the possibility to perform in conditions that polymeric and palladium membranes cannot perform properly thanks to their thermal and chemical stability[179][180]. What's more, it doesn't have concentration polarization problems as PD-Ag membranes do[181]. This new technology is still in its way to be developed, but some studies have concluded that their low production and material costs and high efficiency regarding permeance and separation effect will make this technology to be one of the most interesting gas separation technology in the field of membranes[179]. One of the application for which CMSMs are been investigated is steam separation from gaseous streams which could be beneficial for CO<sub>2</sub> revalorization processes or CO<sub>2</sub> separation from biogas for its upgrading[182][183].

Carbon molecular sieve membranes (CMSM) are formed by unorganized microstructures and studies have determined that the separation performance of the membrane strongly depends on the preparation of this one[180]. It involves high human involvement on the preparation process and this detail makes this technology more expensive than polymeric membranes[184]. Nevertheless, results are better than the ones obtained from polymeric ones and that's why scientists are working on this technology currently[185].

This kind of membranes are used for gas separation, for example, H<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub> or CO<sub>2</sub>[186]. Figure 15 shows the permeability of the carbon membrane for each gas. As it can be seen Hydrogen gas has the highest permeability through a CMSM, but consequently its selectivity could result not being as satisfying. Still CMSM are regarded to be advantageous for both permeability and selectivity compared to polymeric ones[184].

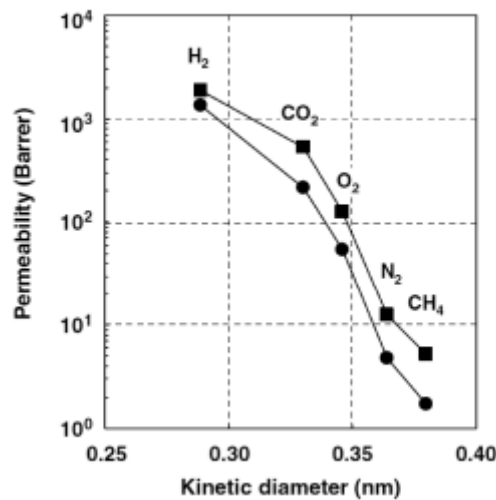


Figure 15 – Single gas permeabilities of C(PPO) (circle) and C(TMS80) (square) as function of the gas molecules kinetic diameter at 298 K.[184] <sup>7</sup>

Some simulations have been performed in order to see how economically feasible this technology results when obtaining pure hydrogen from a mixture of H<sub>2</sub>-CO<sub>2</sub> gas. SMR is a common process from which hydrogen is obtained and the cost-effective relation as well as reduction of CO<sub>2</sub> emissions are a matter of interest. The structure of the membrane, that is, how the membrane was obtained after a pyrolysis process at a certain temperature has a lot to do on the permeance of this one[186]. The higher is the temperature at which the membrane was manufactured the better results are going to be obtained. Therefore, so that this technology results economically feasible production cost must be reduced.

Not only the temperature at which the CMSM is manufactured has influence on the results, temperature at the reactor or pressure also have consequences. It was demonstrated that the higher was the temperature the higher was the methanol's conversion and hydrogen yield[186]. A study determined[129] that while the Pd-based membrane reactors had the advantage of obtaining a pure hydrogen stream, CMSM achieved higher hydrogen recoveries than the Pd-based ones. What's more, a combination of the two membranes was studied to determine which were the results and it turned out that this configuration had the highest hydrogen recovery compared to the reactor based on each membrane[129].

<sup>7</sup> \*1 Barrer =  $10^{-10} \frac{\text{cm}^3(\text{STP})\text{cm}}{\text{cm}^2\text{s cmHg}}$  (cm refers to the thickness of the material, while  $\frac{\text{cm}^3(\text{STP})}{\text{cm}^2\text{s cmHg}}$  refers to the flux of the gas[210])

However, this kind of membranes, comparing with palladium-based ones, are still in their developing phase for hydrogen purification systems, so no applications are expected in the next years yet. Scientists are still studying how can production cost being reduced[187]. Some studies concluded that becoming economically competitive achieving high purity hydrogen through a carbon hollow fibre membrane is still a challenge due to low mechanical strength for unsupported membranes and complicated membrane reactor design[187][134].

Summarizing what's most important from section 7, the dimensions for membrane reactors shown in the membranes' tables are an approximation based on the information obtained from each of the references in which the diameter and length of the MR were given. Therefore, these volumes have not been considered in the sizing of the onboard energy generation system as there's no certainty that they reflect a real scale onboard energy generation system prototype.

Their efficiencies were calculated from the obtained data as well, where the idea of output energy divided by input energy was applied. These calculations are shown in the appendix.

*Table 12 – Efficiencies corresponding to each membrane reactors*

| MR's efficiencies according to their fuel |     |
|---|-----|
| Methanol                                  | 80% |
| L.Ammonia                                 | 98% |

Membrane reactors (MR) are bulky systems and have been produced for land applications, not being compactness one of their design and manufacturing requirements. One of the key parameters to compare these power systems is the volume that occupies each system. Data for the size of the engines has been included in the review as well as for the FC, but there wasn't found such information for the MR and consequently wasn't included.

MR developers are still working on this technology which is still in its emerging phase. Few information is given on the internet to get an approximation of their real scale size. Nevertheless, some projects are about to be carried out in the next years where MR are going to be part of the propulsion system and will be possible to obtained more detailed information about them.

## **8. TRANSPORT APPLICATIONS**

Each transportation system has its own pros and cons. Onboard hydrogen generation may require steam depending on the carrier considered. Not only this, compared with current energy carriers used in transportation applications (mainly diesel oils), hydrogen carriers require bigger volumes to obtain the same energy. This section aims to present two examples of the maritime and rail sectors as possibilities to apply this technology. They have been chosen based on the available space to allocate the required storage capacity required.

The power systems that are brought up in this review are, from one side, internal combustion engines and proton exchange membrane fuel cells (PEMFC) combined with membrane reactors (MR) fuelled by hydrogen carriers, from the other. For the cases in which carbon dioxide is emitted a carbon storage system was included. This means that for both applications when using methanol, this exhaust gas after-treatment was applied.

As possible applications for these systems, locomotives and bulk carriers were considered. Their space availability makes these power generation systems better suited for them. As it was

mentioned before, the steam reforming of methanol requires water, and a CCS system which will occupy part of the available space. In the case of aviation or automotive transportation, weight limitation hampers the implementation of onboard generation.

Another point to consider these kind of transportation means was the necessity to find a carbon free solution for their power generation. Batteries have been proposed as a solution for these sectors, but power limitations as well as low resistance to moisture or vibrations reduce their chances to success (H.Valentine [188]). Batteries present an instability in the presence of moisture as they embrittle in its presence[189]. According to Don Sadoway [190] [191] moisture destabilize the lithium salts that are used in the electrolyte and generate hydrogen fluoride which consequently causes the degradation of the battery[192]. Therefore, specific batteries are required for marine applications. Nonetheless, the volume and weight in batteries to supply the energy required in a vessel would make unpractical a vessel with long routes powered only by batteries.

Bulk carriers travel long distances and as mentioned batteries have a limited storage capacity for such long distances. Bulk carriers can travel up to 24000 km in some routes which in energy demand turns out to be 50,429 GJ [193]. A lithium-ion battery has an approximate specific energy density of 285 Wh/kg and 785 Wh/L[194], which is 0.001 GJ/kg and 2.826 GJ/m<sup>3</sup>. If a vessel of this kind was powered by a battery, then  $4.922 \cdot 10^4$  Tons or, which is the same, 17,995.08 m<sup>3</sup> of battery would be required.

Another aspect to consider about the proposed bulk carrier could be the prime mover volume. In this study, ICE and FC are considered. In case of ICE the propeller shaft is directly driven by the engine. The engine volume is much bigger than the FC, but in case of FC an electric propulsion system would be required with batteries, electric drives, transformers, etc... Nonetheless, at the moment there are no such big FC available, although FC manufacturers project to make big FC via smaller FC stacks. Considering the volumes required for energy storage, the different of volume in case of ICE and FC can be neglected in comparison with energy storage requirement and the required detail for comparison exceeds the scope of this study. Volumes have been given for each technology through the review so that they can finally be compared and are shown in Table 13.

The volume for the engine corresponding to the bulk carrier is calculated based on the data given by the manufacturer[195]. Height = 12.486 m, Length = 7.522 m and Width = 5.8 m; and therefore a volume of  $H \cdot L \cdot W = 544.74 \text{ m}^3$ . With a rated power of 8340 kW. This volume can be considered as overestimated as it includes the space necessary for servicing the engine, but it has very little impact in the overall volume including the fuel. It is known that two stroke engines are bigger than the ones for locomotives for the same power demand, but the energy demand is bigger for the bulk carriers, therefore, as a consequence the engine volume energy demand ratio will result smaller for the case of the locomotive. This engine is not the one used to calculate the energy demand, because the rated power is smaller than the used one which is 14976 kW. Nevertheless, assuming that the energy demand of a bulk carrier that uses this engine is 50429.024 GJ, the energy demand for a bulk carrier using an engine of 8340 kW is 28083 GJ. Therefore, its corresponding volume energy demand ratio is: 0.0698 L/kWh.

Regarding the fuel tank capacity of a locomotive will depend on the travelling distance that has to complete, as well as the specific fuel consumption and the travelling velocity. Taking into account that the considered locomotive for this review is the diesel hydrodynamic DHD20 locomotive[196] whose engine is the DEUTZ TCD 2013 diesel engine with four cylinders[197], its fuel tank capacity is of 230 L. The total energy demand in this case is 4.3 GJ, so therefore the space occupied by the battery system would be of 1.52 m<sup>3</sup>.

The engine's volume for this locomotive is determined in the official webpage of the engine manufacturer Deutz Power Center [197] which is  $0.794 \text{ m}^3 = (A = 1.154 \text{ m}) * (B = 0.694 \text{ m}) * (C = 0.991 \text{ m})$ . Therefore, the corresponding volume energy demand ratio is:  $0.664 \text{ L/kWh} = 794 \text{ L}/1194.4 \text{ kWh}$ . This is shown in Figure 16.

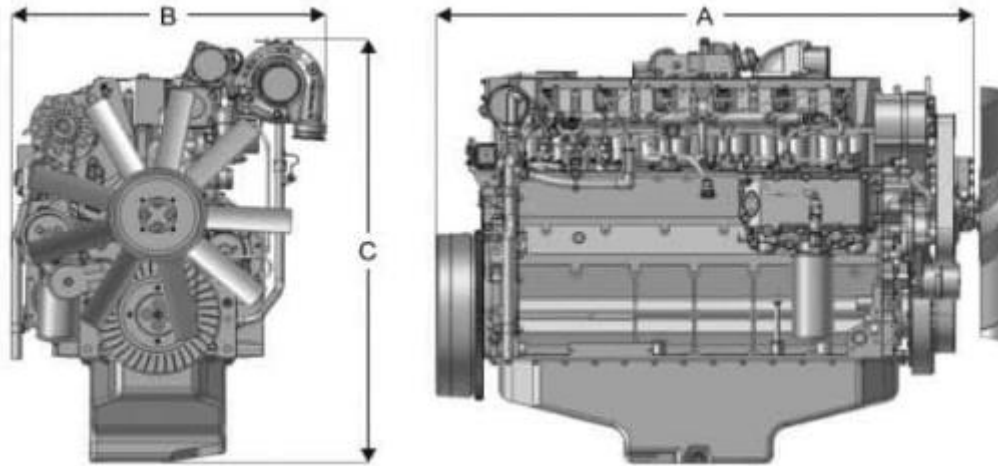


Figure 16 – Deutz power engine

This review aims to replace these mentioned engines with two possible onboard energy generation solutions, 1) Engines for alternative fuel combustion (hydrogen carriers) 2) Membrane Reactors together with PEMFC for hydrogen carriers. In order to make a comparison between these systems, two aspects have been taken into account: efficiency of each technology and occupied space. The previous sections were intended to provide both general information about these technologies as well as efficiencies and sizing specifications.

Due to this lack of available information about the sizing of the membrane reactors, it has not been possible to consider Membrane Reactor's volume in the comparison. As a consequence, neither the volumes of the fuel cells or engines have been included. To make the comparison of the occupied volumes the sizes of each fuel tank as well as their corresponding water supply or CCS tanks if needed were considered.

As an example, a bulk carrier powered by a steam methanol reforming process through membrane reactors and fuel cells would require around  $28,257.49 \text{ m}^3$  for the case of steam reforming of methanol where the considered volumes are the water supply tank, the CCS system and the methanol fuel tank and  $9,658.84 \text{ m}^3$  for the decomposition of ammonia where the considered volumes include ammonia fuel tank. In case of ships, there is also the option to generate fresh water on board from seawater via desalination processes already available and used in ships. So, in some cases the water supply tank volume might be reduced if such systems are implemented on board.

Table 13 summarizes the mentioned properties corresponding to each technology. The volume ratio is the volume of the technology divided by the total energy demand of the transportation means. As a consequence of not having the volumes for membrane reactors, this characteristic is not included in the table. The volume energy ratio for diesel engine corresponds to the engine and energy demand of the locomotive.



Table 13 – Volume energy ratio and efficiency for each technology

| Technology       | Efficiency %    | Volume L/kWh                            |
|------------------|-----------------|---|
| Diesel Engine    | 53.00%          | Locomotive 0.664<br>Bulk Carrier 0.0698 |
| Methanol Engine  | 51.86%          | 0.0102                                  |
| Ammonia Engine   | 38.75%          | -                                       |
| Hydrogen Engine  | -               | -                                       |
| Fuel Cell        | ~50%            | 0.76                                    |
| Membrane Reactor | Ammonia 98.29%  | -                                       |
|                  | Methanol 80.30% | -                                       |

Nevertheless, even if the real scale sizing of the Membrane Reactors is not defined yet, including such technology instead of a reforming or decomposition process (where three to four devices are needed) results more beneficial for the means of transport as the required unit systems gets reduced to one.

We can see this path also in the market. On December of 2021 a Memorandum of Understanding was signed by ABB Marime & Ports[198], Maritime Partners LLC (MP)[110], Elliot Bay design Group (EBDG)[199] and e1 Marine[108] to develop the first methanol reformer hydrogen fuel cell towboat[200]. This vessel is aimed to be fully powered by in situ produced electricity from the reforming of methanol and hydrogen powered fuel cells though a traditional reforming process. It was determined that less carbon dioxide emissions were associated with this power system than with a diesel engine one. This posed a clear advantage for reducing emissions coming from this sector.

The energy consumption reduction has also been a strength for this hydrogen onboard generation system, which e1 Marine has claimed that consumes 35% less energy than diesel generators[201]. Considering that membrane reactors obtain similar results to traditional reforming processes but with a single unit at lower temperatures, membrane reactors seem to be an alternative for onboard energy generation. Although this shows the need to develop specific Membrane Reactor for transportation application.

The downside about producing onboard energy through membrane reactors and then with Fuel Cells is that Fuel Cells have a limited power of around 250 kW[100] while the mentioned bulk carrier has a power demand of 14976 kW. This means that this bulk carrier would require 60 fuel cells to supply the required power for it. Nevertheless, fuel cell stacks developers are improving their power capability[202]. Nonetheless, FC-s will require an entire electric propulsion system on board (electric motors, drives, transformers, distribution system, etc...), while a two stroke engine has a very simple propulsion system that directly drives the propeller from the engine with a simple shaft.

Considering everything mentioned above, membrane reactors together with fuel cells offer an alternative power generation for locomotives and bulk carriers that avoid carbon emissions. The methanol's steam reforming process needs a CCS system and a water supply and therefore is not such an attractive solution. In the case of ammonia's decomposition there's no such a need to

include these two, and therefore this onboard generation system seems to be an appropriate solution for locomotives and bulk carriers. The only drawback is the power limitation of the fuel cells which after literature research no power greater than 250 kW was found.

## 9. DISCUSSION

This review aims to compare two onboard power generation systems based on hydrogen and other hydrogen carriers for heavy means of transportation. Hydrogen's application in the transport system still remains in its emerging phase and scientist are coming up with different solutions for its application. In this sense, one of the main challenges is the onboard storage and transportation of this fuel.

After literature research, in which many different parameters have been considered, such as energy consumption when converting it into a carrier or hydrogen content per volume unit, it was concluded that the best options among the considered ones to storage hydrogen were as methanol and liquid ammonia. As it can be seen in Figure 17, their high hydrogen content and low energy consumptions when converting hydrogen into hydrogen carrier makes these two carriers the best solutions to storage hydrogen onboard.

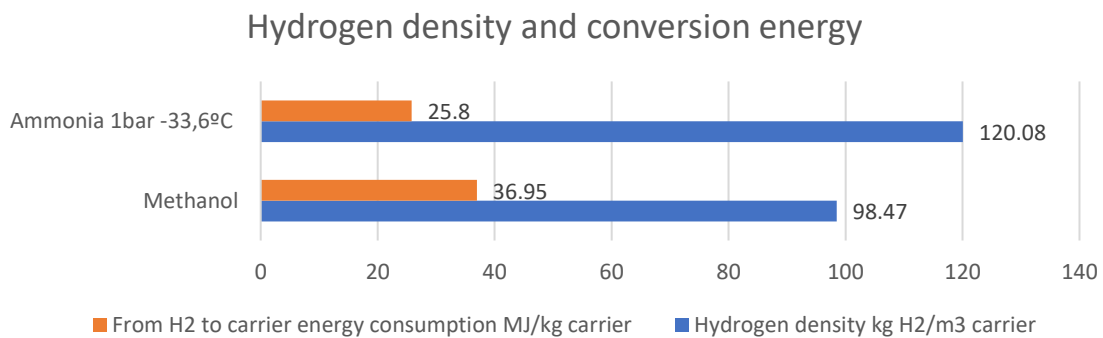


Figure 17 - Hydrogen density kg H<sub>2</sub>/m<sup>3</sup> and conversion energy MJ/kg<sup>8</sup>

The emissions related to each of the applications were also studied for these carriers and it was determined that methanol's steam reforming process and methanol's combustion in an ICE would require a CCS system in order to avoid GHG emissions to the atmosphere. As a result, an energy consumption corresponding to this system was included when calculating the global efficiency for each of the power generation systems. It wasn't included the energy consumption for the exhaust gas NO<sub>x</sub> after-treatment as this system is already included in most of the vehicles nowadays and their energy consumption can be neglected because they are also necessary in case of methanol combustion in ICE to meet the strictest NO<sub>x</sub> limits.

There were mainly three technologies that were analysed in this review, Internal Combustion Engines, Membrane Reactors and Fuel Cells. For each of these technologies' efficiencies were obtained to make a comparison between them and suggest which could be the best solution. For internal combustion engines depending on the applied fuel different energetic efficiencies were obtained. Methanol's combustion has an approximate efficiency of 51.86% and ammonia's combustion an efficiency of 38.75%. For the case in which hydrogen is combusted there was no information found about the efficiency of an engine when this fuel was applied, therefore this data couldn't be compared. This is due to the fact that using hydrogen as a combustion fuel is still in study phase and it has only been used as an enabler to improve the combustion of those fuels that

<sup>8</sup> Used equations are shown in the appendix

have more difficulty to start burning. In any case, we can assume that it would not be far from the efficiency obtained with Ammonia in case of SIE application.

In case of direct combustion of ammonia in ICE it has the simplest layout as the ammonia could be directly fed to the ICE eliminating many components and systems between zero-carbon fuel and end user (the ICE). But using ammonia in ICE still poses a very important challenge and would not be a pure zero GHG solution as it would need lubricating oil that emits carbon when burnt and pilot injection of diesel-oil in case of dual fuel engine. Depending on the source of diesel oil this could mean also emission of GHG. Not only this, ammonia combustion is a source of very harmful emissions, NOx and N2O that could offset benefit of zero carbon fuel if not addressed correctly.

Regarding the efficiencies for the membrane reactor, it was calculated as the ratio between the useful energy and the energy input to the system. The useful energy corresponds to the permeated hydrogen through the membrane while the introduced energy corresponds to the introduced carrier. To calculate the permeated hydrogen, conversion rates and hydrogen recoveries were used. The efficiencies corresponding to a membrane reactor to obtain hydrogen from methanol and ammonia were 80.3% and 98.29% respectively.

Lastly regarding the efficiency of fuel cells, after literature research, it was determined that the efficiency of Proton Exchange Membrane Fuel Cell is 50% approximately. This data is gathered in Figure 18.

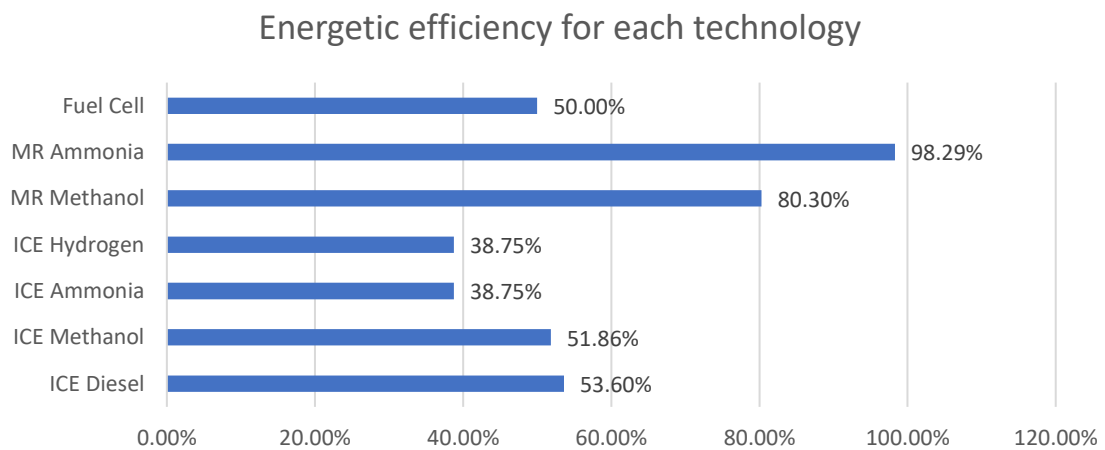
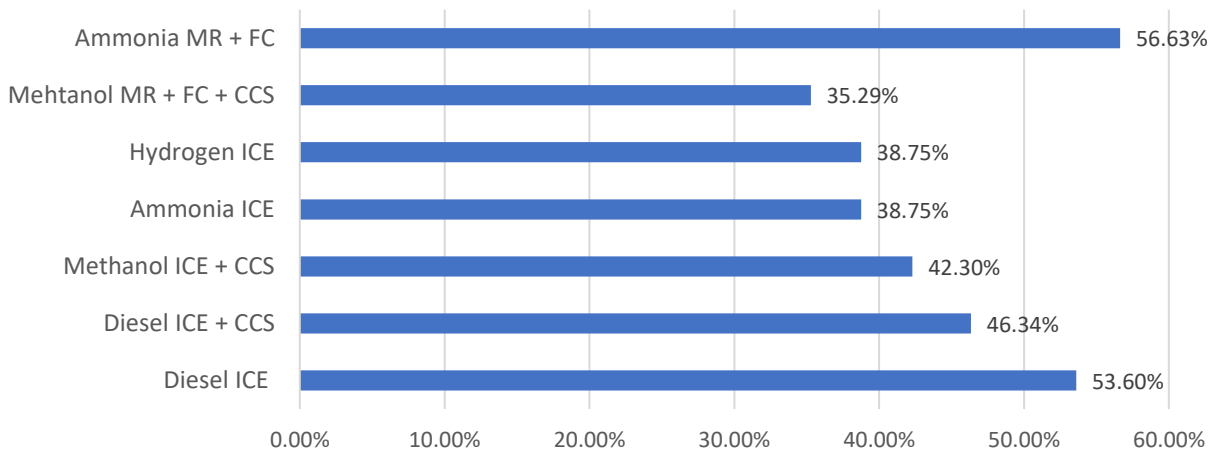


Figure 18 - Energetic efficiency for each technology.

Once all the efficiencies were calculated, in order to compare the onboard energy generation systems, it was calculated the global efficiency of each generation systems. This data is shown in Figure 19. On the one hand, efficiencies corresponding to the ICE ended up being 42.3% for methanol and 38.75% for ammonia. On the other hand, for the combination of membrane reactors and fuel cells, the corresponding efficiencies were 35.29% for methanol and 56.63% for ammonia. Efficiencies corresponding to the energy solutions related to methanol ended up being lower than expected. This low global efficiency result is because of the energy consumption of the CCS system. As ammonia doesn't have any carbon in its molecule, no CCS was required and therefore less energy was demanded. This aspect gives this onboard energy generation system based on ammonia an advantage in comparison to the other proposed systems.

## Global energetical efficiency for each onboard energy generation system



*Figure 19 - Global energetical efficiency for each onboard energy generation system.<sup>1</sup>*

Nevertheless, another aspect to consider apart from energy efficiencies was also the volume occupancy for each onboard energy generation system. For the methanol’s steam reforming process, water supply was included which enlarged the volume demand for this energy solution. The CCS system also had a volume occupancy that couldn’t be ignored. Regarding the volumes for membrane reactors, no such data was found and therefore volumes corresponding to engines, membrane reactors and fuel cells were not included in the final occupied volume calculated for each power generation solution. Table 14 summarizes the occupied volume of each fuel for each onboard energy generation solution to supply the energy demand of the bulk carrier and the locomotive.

*Table 14 – Volume occupancy for each fuel and onboard energy generation solution*

| Volume Requirement for each transport system m <sup>3</sup> |            |          |
|---|------------|----------|
|   | Locomotive | Vessel   |
| Power kW  | 173        | 14976    |
| Energy Demand GJ  | 4.305      | 50429    |
| Diesel  | 0.23       | 2352.00  |
| Diesel + CCS  | 0.96       | 11215.05 |
| Ammonia ICE   | 1.21       | 14116.65 |
| Ammonia MR + FC   | 0.82       | 9658.84  |
| Methanol ICE + CCS  | 1.53       | 17892.48 |
| Methanol MR + CCS + FC                                      | 2.41       | 28257.49 |

For the volumes corresponding to the storage of the fuels, tank volume/stored fuel volume ratios were considered. For the case of storing liquid ammonia, three ratios were obtained, in which each of the ratios vary slightly between them. Therefore, the average ratio was used. The mentioned tank/liquid ratios are: 1.4665 m<sup>3</sup>tank/ m<sup>3</sup> liquid ammonia [203], 1.4 m<sup>3</sup>tank/ m<sup>3</sup> liquid ammonia [152] and 1.27 m<sup>3</sup>tank/ m<sup>3</sup> liquid ammonia [204]. The ratios that were considered for the storage of methanol 1.424 m<sup>3</sup>tank/ m<sup>3</sup> for a 1000 Gallon methanol storage tank [205] and 1.373 m<sup>3</sup>tank/ m<sup>3</sup> for a 10000 Gallon methanol storage tank [206]. This data was provided by General Industries Inc. [207].

Membrane reactors are still emerging and until a prototype for its use is developed, this volume requirement won't be specified. Tecnalia together with the university of Eindhoven are working on this technology and recently a spin-off company, H2SITE[208], has been created aiming to apply membrane reactors to obtain pure hydrogen onboard in the most efficient way. The volume demand for each system per energy demand was: 0.56 m<sup>3</sup>/GJ for the SMeR, 0.355 m<sup>3</sup>/GJ for ICE of methanol, 0.191 m<sup>3</sup>/GJ for decomposition of ammonia and 0.28 m<sup>3</sup>/GJ for ICE of ammonia. It must be considered that all these were research projects with very bulky installations designed to ease modifications and tests and not industrial reactors focused for transportation applications.

Volume requirement for each transport system relative to diesel tank

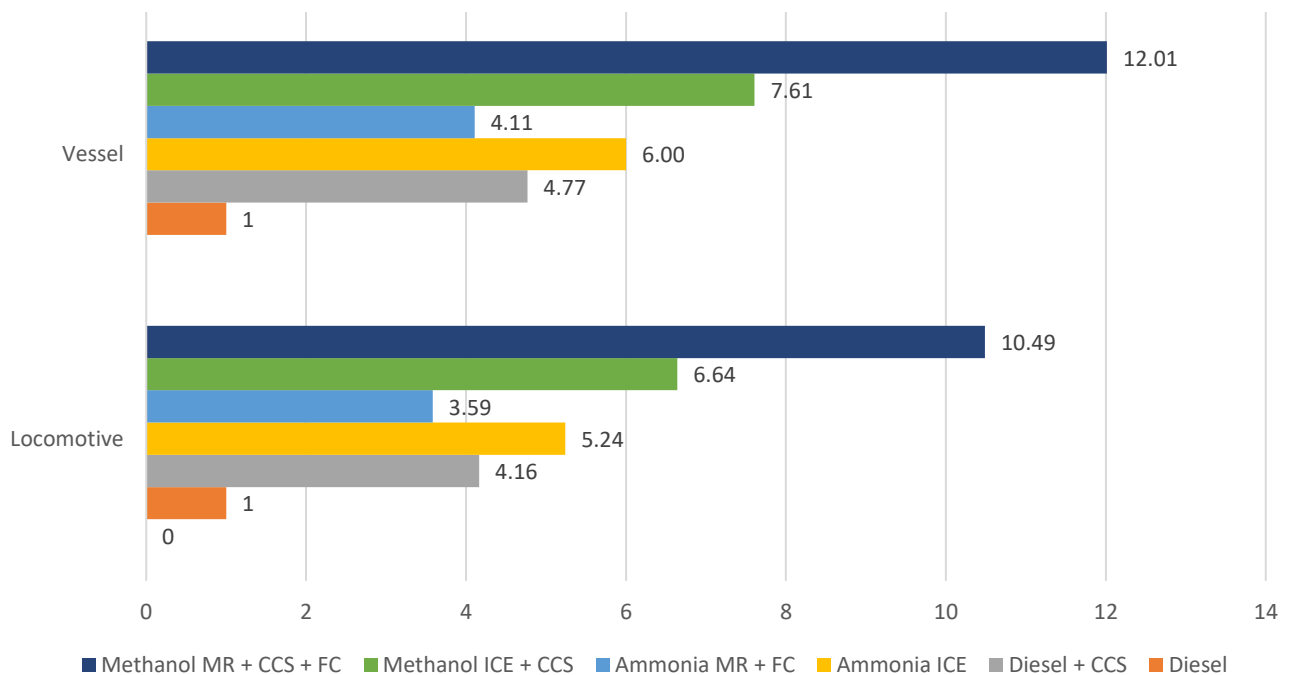


Figure 20 – Volume requirement for each transport system relative to diesel tank

Finally, taking into account Figure 20 –where the volume requirement for each transport system compared to the diesel is given, ammonia decomposition seems to be the most appropriate alternative considering the volume occupied. Ammonia decomposition offers the smallest relative volume occupancy of 4.11 times bigger than the diesel one in the case of the bulk carrier and 3.59 times bigger in the case of locomotive as well as the highest global efficiency with an efficiency of 56.63%. Nevertheless, it is important to remark that the comparison of the volume requirements must be done with the requirement corresponding to the system that includes CCS for the Diesel. It can be seen that the occupied volume for the vessel case is 4.77 times bigger than the Diesel

and therefore bigger than the ammonia decomposition one and 4.16 times bigger for the locomotive case which is also bigger than the one for the ammonia decomposition. Fuel cells and membrane reactors space occupancy wasn't included in the study because of the lack of data.

Considering that the case for which ammonia is used to obtain pure hydrogen through membrane reactors and the generating energy through a fuel cell has the highest efficiency and the smallest volume occupancy per energy demand; it can be concluded that ammonia seems to be the best option to produce energy onboard by means of a membrane reactor combined with a fuel cell. Nevertheless, it can't be ignored the fact that ammonia is a highly toxic hydrogen carrier and it must be kept under rigorous measures to avoid leakages and atmospheric exposure.

## 10. CONCLUSIONS

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This review aims to compare different onboard energy generation systems for heavy means of transport based on hydrogen and other hydrogen carriers. After extended literature research in which several data was gathered, it can be concluded that storing hydrogen as ammonia during the transport to produce energy onboard through membrane reactors together with fuel cells seems to be the most efficient way of onboard energy production among the different studied options.

Nevertheless, membrane reactors are still emerging and haven't been demonstrated at large scale and still have important challenges, especially related to the bulk volume required by the systems. Companies such as H2SITE together with Tecalia and University of Eindhoven are working on this technology to overcome the challenges and introduce them in the energy solution market as soon as possible. Not only membrane reactors have challenges, but also fuel cells need to increase their power capacity so that they can be applied in applications like the ones mentioned in this review.

As an intermediate solution, ICE might offer a feasible solution in a short term, but must also solve the problems associated with the harmful emissions originated in the carbon free fuels like hydrogen and ammonia, emissions especially harmful in the case of ammonia that could offset any advantage of the zero carbon content.

Therefore, membrane reactors combined with fuel cells offer an advantage compared to internal combustion engines when ammonia is applied. The noxious emissions of burning ammonia that could offset any GHG zero emission can be avoided and provide a higher efficiency in the use of available energy. In this way, this energetical solution can become an efficient way to decarbonize the marine and railroad sectors.

## 11. APPENDIX

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### Hydrogen content for each carrier:

$$\frac{H2 \text{ kg}}{\text{carrier kg}} = \frac{X \text{ kmol H2}}{1 \text{ kmol carrier}} * \frac{\text{Molar mass carrier} \frac{\text{kmol}}{\text{kg}}}{\text{Molar mass H2} \frac{\text{kmol}}{\text{kg}}}$$

### Hydrogen volumetric density for each carrier:

$$\frac{H2 \text{ kg}}{\text{carrier m}^3} = \frac{H2 \text{ kg}}{\text{carrier kg}} * \text{Density carrier} \frac{\text{kg}}{\text{m}^3}$$

### Volumetric energy density for each carrier:

$$\text{Volumetric E. Density} \frac{\text{MJ}}{\text{m}^3} = \text{Gravimetric Density} \frac{(\text{LHV})\text{MJ}}{\text{kg}} * \text{Density carrier} \frac{\text{kg}}{\text{m}^3}$$

### Membrane active area of the membrane reactors:

$$\text{Area cm}^2 = \pi * \text{Diameter cm} * \text{Length cm}$$

### Diesel engine's efficiency of a bulk carrier and the required methanol to supply the demanded energy:

To obtain the required methanol demand calculations in EES:

"Bulk carrier energy consumption calculation"

"Design speed considering 15% sea margin, 10% engine margin and 5% propeller light running"

$$SOG = 14.7 \frac{\text{Nm}}{\text{h}} \quad \text{"Design speed in knots"}$$

$$SFOC = 157.2 \frac{\text{g}}{\text{kWh}} \quad \text{"Specific Fuel Oil Consumption in design Speed"}$$

$$NCR = 14976 \text{ kW} \quad \text{"Normal Continuous Rating in design Speed"}$$

$$FOC_{NM} = \frac{(NCR * SFOC * \text{convert}(g, kg))}{SOG}$$

$$LHV = 42700 \frac{\text{kJ}}{\text{kg}} \quad \text{"Lower Heating Value of HFO"}$$

$$Q_{per_{NM}} = FOC_{NM} * LHV * \text{convert}(kJ, MJ) \quad \text{"Energy required in fuel per sailed nautical mile"}$$

"MAN Diesel and Turbo design of the 205,000 DWT bulk carrier would be sailing in a standard route of up to 12,850 nautical miles:"

$$DISTANCE = 12850 \text{ Nm}$$

$$Q_{steaming} = Q_{per_{NM}} * DISTANCE$$

$$Q_{aux_{boilers}} = 0.066 \text{ "6,6\% of total energy"}$$

$$Q_{total} = \frac{Q_{steaming}}{(1 - Q_{aux_{boilers}})}$$

$$Efficiency_{Diesel} = \frac{1*100}{SFOC * convert(g,kg) * convert(\frac{1}{h},\frac{1}{s}) * LHV} \text{ "Diesel engine efficiency"}$$

### "Methanol consumption calculation"

$$LHV_{methanol} = 19900 \frac{kJ}{kg} \text{ "Ref: MAN PROJECT GUIDE, SFOC guarantee conditions"}$$

$$SFOC_{methanol} = 327.6 \frac{g}{kWh} \text{ "Ref: MAN PROJECT GUIDE, SFOC guarantee conditions at 75\% load, Tier III mode"}$$

$$SFOC_{pilot} = 9.9 \frac{g}{kWh} \text{ "Pilot diesel injection"}$$

$$Efficiency_{Methanol\%} = \frac{1 * 100}{(SFOC_{methanol} * LHV_{methanol} + SFOC_{pilot} * LHV) * convert(g,kg) * convert(\frac{1}{h},\frac{1}{s})}$$

"Methanol engine is Dual Fuel Engine. Requires diesel pilot injection for ignition."

$$Ratio_{diesel_{energy}} = \frac{SFOC_{pilot} * LHV}{SFOC_{methanol} * LHV_{methanol} + SFOC_{pilot} * LHV}$$

$$Q_{steaming_{methanol}} = Q_{steaming} * \frac{\eta_{diesel}}{\eta_{methanol}} \text{ "Energy demand for the methanol fuelled system"}$$

"Methanol engine has some lower efficiency"

$$V_{methanol_{energy}} = 15647 \frac{MJ}{m^3} \text{ "Methanol volumetric energy content"}$$

$$V_{methanol} = \frac{Q_{steaming_{methanol}}}{V_{methanol_{energy}}} \text{ "Total methanol volume required for steaming"}$$

### **SOLUTIONS**

$$Density_{FO} = 875 \frac{kg}{m^3}$$

$$\eta_{diesel} = \mathbf{0.5363}$$

$$FOC_{NM} = 160.2 \frac{kg}{Nm}$$

$$FOC_{weight} = 2.058 * 10^6$$

$$LHV_{methanol} = 19900 \frac{kJ}{kg}$$

$$Q_{aux_{boilers}} = 0.066 \text{ MJ}$$

$$DISTANCE = 12850 \text{ Nm}$$

$$\eta_{methanol} = \mathbf{0.5186}$$

$$FOC_{volume} = 2352 \text{ m}^3$$

$$LHV = 42700 \frac{kJ}{kg}$$

$$NCR = 14976 \text{ kW}$$

$$Q_{per_{NM}} = 6838 \frac{MJ}{Nm}$$



$$Q_{steaming} = 8.78 * 10^7 MJ$$

$$Q_{steaming_{methanol}} = 9.088 * 10^7 MJ$$

$$Q_{total} = 9.408 * 10^7 MJ$$

$$Ratio_{diesel_{energy}} = 0.061$$

$$SFOC = 157.2 \frac{g}{kWh}$$

$$SFOC_{methanol} = 327.6 \frac{g}{kWh}$$

$$SFOC_{pilot} = 9.9 \frac{g}{kWh}$$

$$SOG = 14.7 \frac{Nm}{h}$$

$$V_{methanol} = 5808 m^3$$

$$V_{methanol_{energy}} = 15647 \frac{MJ}{m^3}$$

### Feed flow rate:

$$Feed\ flow\ rate \frac{mol}{s} = WHSV h^{-1} * Catalyst\ weight\ kg * \frac{1\ mol\ carrier}{X\ g\ carrier} * \frac{1h}{3600\ s}$$

WHSV: Weight Hourly Space Velocity

### Load to surface ratio:

$$Load\ to\ surface\ ratio \frac{mol}{s * cm^2} = \frac{Feed\ flow\ rate \frac{mol}{s}}{Membrane\ area\ cm^2}$$

### Energetic efficiency for Membrane Reactors:

$$Conversion\ \% = \frac{Reacted\ carrier}{Introduced\ carrier} * 100$$

$$Produced\ hydrogen = Reacted\ carrier * hydrogen\ content\ in\ the\ carrier$$

$$Hydrogen\ recovery\ \% = \frac{Permeated\ hydrogen}{Produced\ hydrogen} * 100$$

$$Membrane\ Reactor\ Efficiency\ \% = \frac{Permeated\ hydrogen * LHV\ H2}{Introduced\ carrier * LHV\ carrier} * 100$$

### Global efficiency for each energy generation system:

$$Global\ Efficiency\ \% = \frac{Usefull\ energy}{Introduced\ Energy\ in\ the\ system} * 100$$

$$Introduced\ E. = Introduced\ Carrier * LHV\ carrier + CCS\ energy\ consumption$$

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