Department of Mechanical and Aerospace Engineering

Investigation of renewable fuels for a Scottish ferry service

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Abstract

Although the international shipping sector is responsible for 2.5% of the global GHG emissions, it is exempted from the Paris Agreement because their emissions are considered as not country related (ICTSD, 2018). Regulations for emissions are insufficiently and efforts towards sustainable propulsion concepts lacking. This thesis investigates potential shipping fuels for a Scottish ferry service. Only fuels which can be produced by renewable resources are considered.

The overall aim is to reduce GHG emissions and to promote sustainable propulsion concepts in the shipping sector. The main focus is on the creation of a tool to calculate and validate key figures, such as conversion efficiencies, storage capacity and environmental impacts. Objectives include compliance with basic requirements such as propulsion power, range and appropriate tank size. Furthermore, health and safety issues must ensure the safety of passengers on the vessel at any time. Savings in GHG emissions and environmental impact of fuel production are part of the desired results.

Even if the developed tool is supposed to be applicable for different vessels with different requirements, the report only deals with a specific vessel operating on the route between Oban on the Scottish mainland and Castlebay on the Isle of Barra. The calculations in the tool are exclusively based on research results and many assumptions have been taken to achieve reasonable results.

The discussion considers the results in a broader scope and deals with pro and cons of each fuel. Three of the most promising fuels, including ammonia, hydrogen and methanol, are investigated in detail. Some of the basic findings include poor efficiency of ammonia utilisation, massive space requirements for hydrogen storage and little emission savings if methanol is used as a fuel. However, technical feasibility and fewer challenges as might be expected can be proven.

Acknowledgements

First, I would like to thank my supervisor Dr Paul Tuohy, who continuously supported me with valuable input and always answered my questions very comprehensively. It is also due to him that I became aware of this topic and an ongoing hydrogen ferry project to the Hebrides. I am also grateful to Ms Leanne Bloor from Wood Group, who provided me with some information about current research, which helped me to specify and narrow the scope of this work. Furthermore, I would like to thank Mr David Hogg from the Bright Green Hydrogen. He kindly invited me to visit the hydrogen test site in Methil, to see hydrogen production facilities and to talk about ongoing hydrogen projects. Lastly, I would like to thank my beloved girlfriend for her support and patience during a stressful time.

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List of Abbreviations

AFC	alkaline fuel cell
ASU	air separation unit
CH3OH	methanol
CNG	compressed natural gas
CO2	carbon dioxide
DI	direct injection
DME	dimethyl ether
DMFC	direct methanol fuel cell
ECA	emission control area
GHG	greenhouse gas
HCCI	homogeneous charge compression ignition
HFO	heavy fuel oil
H2	hydrogen
H2O	water
IMO	International Maritime Organisation
LNG	liquid natural gas
LPG	liquefied propane gas
LPG	liquid petroleum gas
MDO	marine diesel oil
MeOH	methanol
MVC	mechanical vapour compression
NH3	ammonia
NH4+	ammonium
NOx	nitrogen oxides

OH	hydroxide
PEM	proton-exchange membrane
PEMFC	proton-exchange membrane fuel cell
ROC	renewable obligation certifications
ROPAX	roll-on/roll-off passenger ferry
ROC	renewable obligation certificates
SOFC	solid oxide fuel cell
SOx	sulphur oxides
TDC	top dead centre

1. Introduction

1.1. Background

“Look deep into nature, then you will understand everything better.”
(Einstein, 1951)

Mankind can always learn from natural processes which are often very efficient and mature. In his work on the photoelectric effect, Albert Einstein revealed, that sunlight can be harnessed to push electrons for electricity generation. Based on this, it took scientists and engineers almost a century to make the conversion of sunlight into electricity at least 22% efficient (Aggarwal, 2018). The total solar energy continuously reaching the earth’s surface is 10,000 times the world’s total energy use (Chandler, 2011). However, the production of solar electricity is intermittent and depends on the location, the climate and the daytime, which makes it impossible to deliver a constant power. This so-called non-dispatchable energy resource also applies to wind energy which is dependent on the highly fluctuating wind occurrence. The exact production of power cannot be predicted in advance. Indeed, it is not possible to completely rely on non-dispatchable energy resources but with storage opportunities and grid balancing mechanisms, a sustainable and carbon-free energy system might be possible.

Although the electricity sector has changed appreciable towards renewable resources, the transport sector is still strongly depending on fossil fuels. Approximately 20% of the global greenhouse gas (GHG) emissions are caused by the transport sector including road, air and marine traffic. The European target implies that GHG emissions from transport must be reduced by 60% by 2050, compared to the level of 1990 (European Commission, 2011). It cannot be assumed that transport will decline within the next decades, therefore, working on solutions to make the transport sector cleaner and more sustainable is crucial. In the short term, battery technologies might be a good choice for cars and small vehicles with limited requirements of range. Eventually, it will not be the best solution at all, because of insufficient resources such as lithium or rare earth elements and limited recyclability.

Rail traffic is highly electrified with a good carbon footprint if renewable electricity is used. However, air and marine traffic are still very conservative using a similar technology for decades. Aeronautical engineers struggle with energy densities and power to weight ratios of non-conventional fuels, being crucial factors for the entire aircraft design. It is not very different in marine engineering, but the weight factor is less important, and vessels have much more capacity for storage than aircrafts. Emission regulations in shipping industry though are amongst the poorest of all industries and the need for action appears urgently in this sector.

In the long term, low-fossil-carbon fuels or even carbon-free fuels which can be produced by renewable electricity and non-fossil resources such as water, biomass or captured carbon dioxide (CO2), might be not only a solution for the entire transport sector but also for balancing intermittent electricity for a stable grid. They can be either combusted in adjusted conventional engines or in fuel cells providing electrical energy. Even if the round-trip-efficiencies are still in lower double figures, prospects for easily transportable fuels, based on non-fossil resources with a significant reduction in GHG emissions, are very bright and developments just at the beginning.

1.2. Aim and Motivation

This thesis aims to analyse the suitability of renewable fuels for vessels in ferry service to Scotland's remotest island communities. Using only renewable electricity and abundant natural resources to produce fuels, it is supposed to be a sustainable and carbon-neutral solution for powering large vessels of the cruise ferry or roll-on/roll-off passenger (ROPAX) category. The thesis seeks to support the study conducted by several stakeholders including leading private sector companies and the Scottish Government. The findings of this paper might have some valuable impact on the further development and the realisation of a pioneering marine engineering project.

The motivation of the project is first and foremost the reduction of carbon emissions to meet the Scottish target of reducing emissions by 80% by 2050, including emissions from international aviation and shipping (Scottish Government, 2016). However, it is not about meeting targets but rather changing the energy supply to a more efficient and long-term affordable system with abundant resources for the next generations. Another crucial point is the independence of fossil fuels and their expensive explorations. Renewable resources such as solar, wind or hydro are for free and with access for everyone around the world. There is no place on earth without any chance to harness energy from nature. The shipping sector, in particular, is far away from being sustainable. Therefore, it is even more important to do research and development in this field of technology. Synthetic fuels produced by renewable energies appear to be a possible solution for large ships being carbon free or at least carbon neutral.

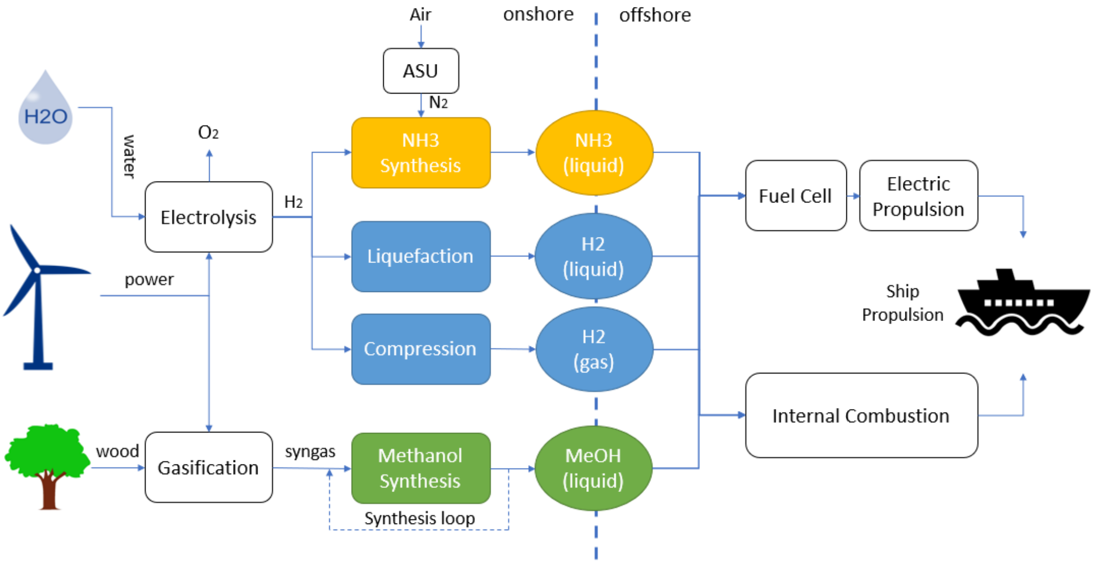


Figure 1: Overview of fuel options and its main conversion processes (Source: Own design).

Figure 1 gives an overview of the core investigation in this work. Comparing three of the most promising fuels based on renewable resources for its application in shipping. Later described in detail, the tool provides comprehensive results on system efficiency, fuel consumption, required storage capacity and environmental impact in accordance to predefined propulsion requirements for a specific vessel. A more detailed description of this graph is explained in Chapter 5.

1.3. Project Objectives and Scope

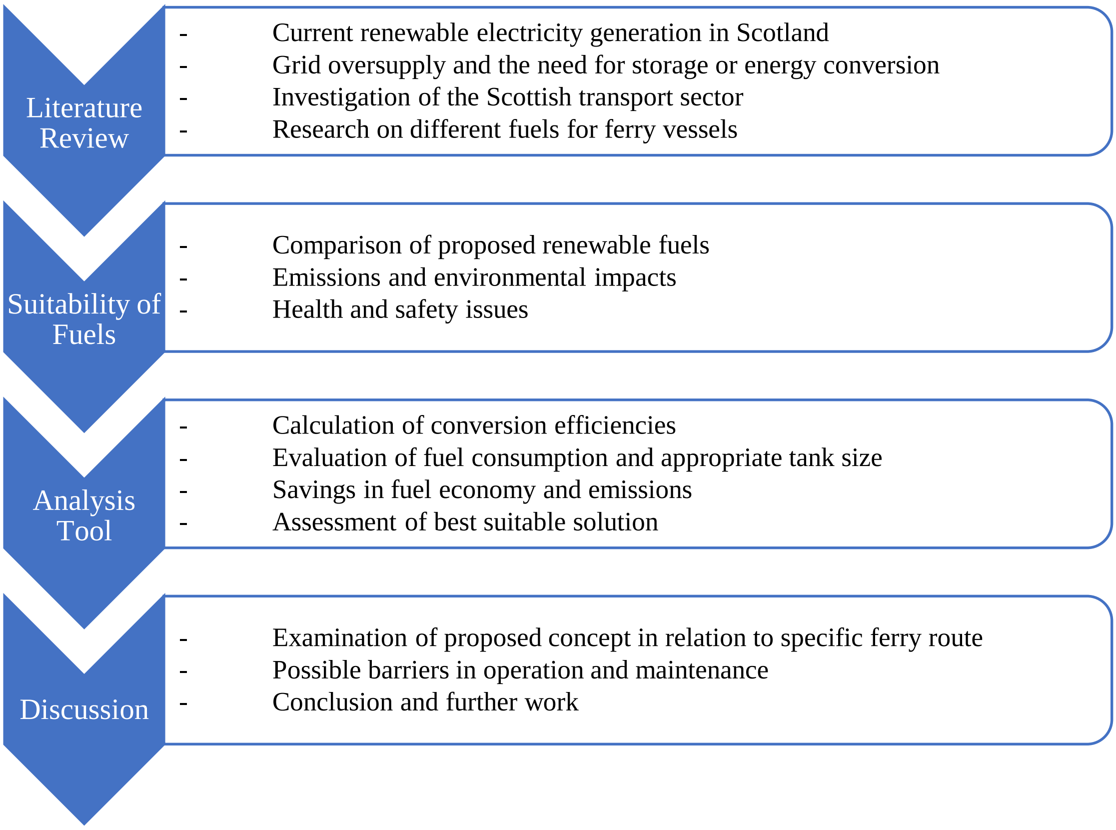
The main objective of this work is to investigate the best suitable fuel for a Scottish ferry service and its feasibility to power ships of the size currently in operation.

- Meeting all requirements for a ferry vessel including adequate range, appropriate tank size, low maintenance and good reliability.
- Significant reduction of GHG emissions compared to the current ship in service.

- Proof that ships can run sustainable and independent of fossil fuels without massive adjustments in design.
- Satisfy all the health and safety requirements on sea-going vessels.
- Evaluation and discussion of necessary infrastructure adjustments.

The report will not consider any detailed economic aspects due to the hardly predictable costs of such a new and unmatured market. Out of scope is also the ship propulsion design especially the mechanical and electrical components. This paper is supposed to be more a feasibility study of renewable fuels for ferry vessels than a ship design project.

1.4. Methodology



Literature Review
- Current renewable electricity generation in Scotland
- Grid oversupply and the need for storage or energy conversion
- Investigation of the Scottish transport sector
- Research on different fuels for ferry vessels

Suitability of Fuels
- Comparison of proposed renewable fuels
- Emissions and environmental impacts
- Health and safety issues

Analysis Tool
- Calculation of conversion efficiencies
- Evaluation of fuel consumption and appropriate tank size
- Savings in fuel economy and emissions
- Assessment of best suitable solution

Discussion
- Examination of proposed concept in relation to specific ferry route
- Possible barriers in operation and maintenance
- Conclusion and further work

Figure 2: Methodology of thesis (Source: Own design).

The first section provides relevant knowledge about the Scottish energy generation, curtailed wind power and basics about different renewable fuels. Special attention is paid to the conversion of electricity into fuels as it is a complex and new area of technology and a moderate understanding is necessary to conduct further studies.

The following chapter compares proposed fuels and validates their suitability in conventional engines. The section comprises the findings from the literature review and comes up with a proposed solution. Considerations of emissions and environmental impact will be listed in a table. It will also include key figures for the analysis section. Health and safety concerns are also discussed as these have some influence on choosing the appropriate technology.

The analysis section consists of a tool showing all the necessary conversion steps from power-to-fuel and fuel-to-power, with efficiencies, energy consumption, storage and feedstock requirements as well as carbon emission savings.

The final chapter validates the results and provides a detailed description of the proposed solution including a description of how to implement it in a real project and what problems and barriers may occur. Furthermore, a clear statement about the feasibility of the proposed concept is given and it is mentioned what further work needs to be done for a successful project realisation.

2. Literature Review

2.1. Renewable Energy in Scotland

2.1.1. Current State and Prospects

Scotland is one of the leading nations in renewable energy generation worldwide. In 2017 around 68% equalling 25 TWh of electricity consumption was based on renewable sources (Scottish Government, 2018). The rate of increase is incredibly and has more than doubled within the last 7 years (see Figure 3). The Scottish target of reaching 50% renewable electricity by 2015 has exceeded and the upcoming target of producing 100% of gross electricity consumption by 2020 seems to be achievable. However, that does not mean, that Scotland is able to entirely rely on renewable electricity. The export rate of domestic power generation accounts of 29%, i.e. energy need to be transmitted to England and Northern Ireland due to oversupply (Government Scotland, 2016). At other electricity must be imported to cover all the demand.

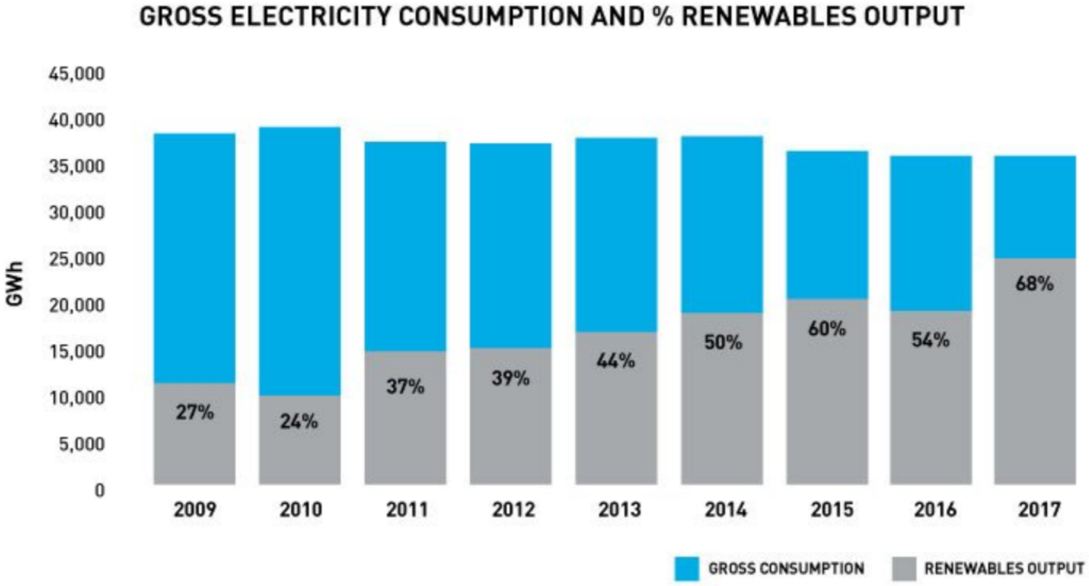


Figure 3: Electricity consumption Scotland (Scottish Government, 2016).

The largest contributor to renewable electricity production in Scotland is wind power with around 17 TWh in 2017. Its share adds up to roughly two-third of all renewables and could provide electricity for around 400,000 homes. Mainly because of climate conditions and the geographical location the share of wind energy is exceptionally high and other renewable resources such as solar energy contribute less.

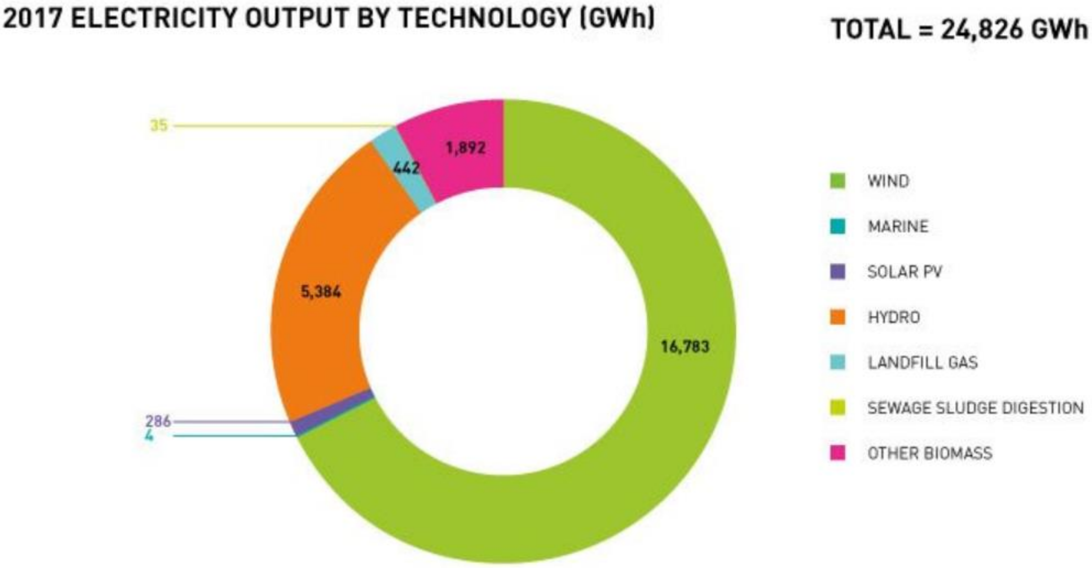


Figure 4: Power output by technology (Scottish Government, 2018).

In 2017, Scotland had 9.7 GW of installed renewable electricity generation capacity and additional 11.6 GW of projects under construction or consented. Another 2.9 GW are in planning stage accounting for 21.3 GW of power capacity based on renewable resources (Scottish Government, 2018). Comparing this amount to the peak load in the UK in 2017, Scotland would be able to cover the entire UK's demand by at least 40%, just using renewable resources (World Nuclear Association, 2018). However, non-dispatchable resources such as wind or solar energy are characterised by over- and undersupply. Therefore, compensation facilities or energy storage options need to be applied to meet the demand constantly. Furthermore, it is necessary to build the infrastructure to transmit and distribute the power, as otherwise the available capacity cannot be used, and facilities need to be costly switched off. The following section describes the importance of sufficient grid capacity more in detail.

2.1.2. Grid Capacity

Scotland's target to be 100% renewable in electricity generation by 2020 is the most ambitious one in the EU (Scottish Government, 2016). The greatest potential to reach the target lies in wind power, particularly in offshore wind power. Several offshore wind farm projects are in planning or under construction. The infrastructure to transmit and distribute the energy to the mainland and to dense populated areas is one of the challenges to cope with. From a technical perspective the transmission losses are crucial and the limiting factor for distances. However, the economic barriers, in terms of the high costs for transmission lines, are more significant. In the countryside, the lines also disturb the visual landscape and residents are mostly against it. The more capacity installed, the larger and costlier the transmission lines. The best wind conditions are in the remote parts of Scotland in the North and West. The connections to the large cities are very poor though. Without appropriate transmission lines, the distribution of power from remote wind farms is not feasible. Figure 5 shows the electrical grid in Scotland with power flow directions. The size of arrows represents the amount of energy transmitted and it appears that the transmission lines to the coastal areas in the West are very deficient. Thus, plans to transmit or storage and distribute the remotely produced electricity are urgently required (National Grid, 2017).

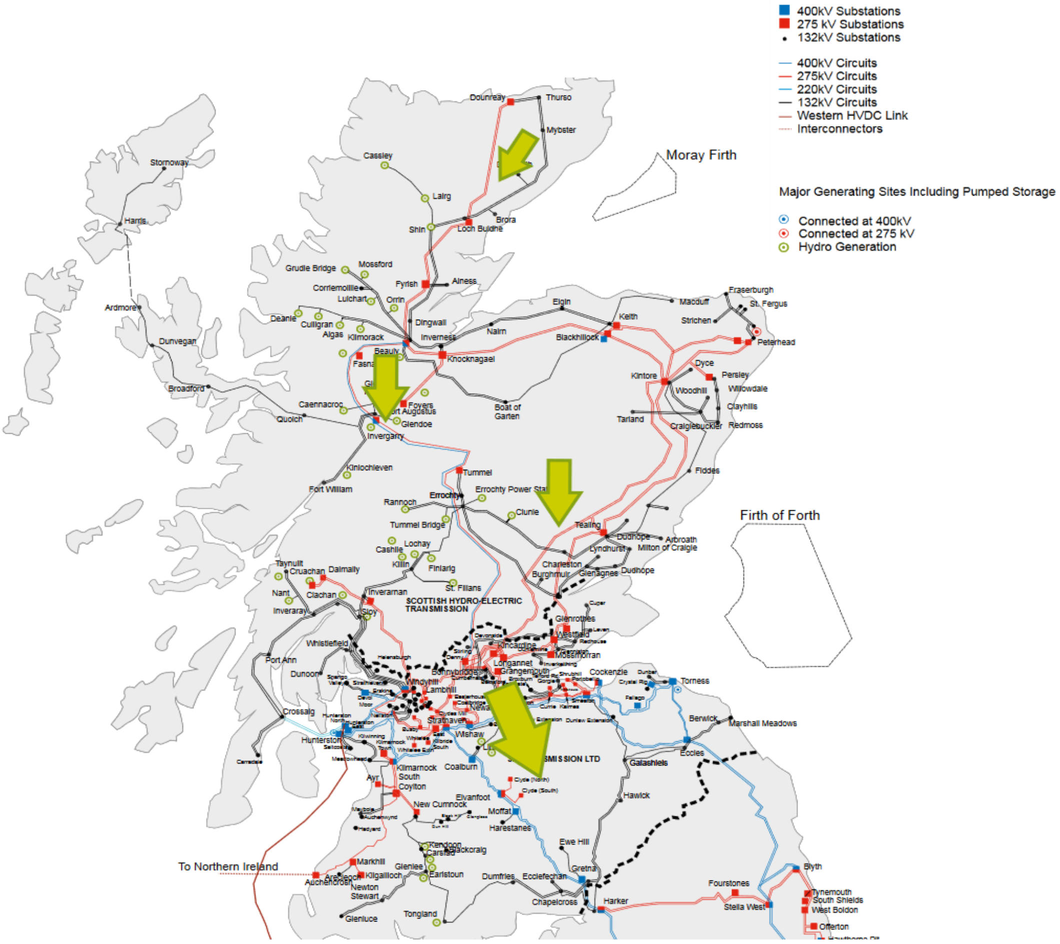


Figure 5: Power grid Scotland (National Grid, 2017).

Western Isles Connector

The Scottish energy company SSE has been planning to lay a subsea cable between Gravir on the Isle of Lewis to Ullapool on the Scottish mainland (see Figure 6). The planned 320 kV line should support the existing 33 kV line between the Isle of Harris and the Isle of Skye (4C Offshore, 2018). Furthermore, it should create the necessary infrastructure to export wind power from the proposed projects on Lewis with planning permission for 118 MW near Stornoway and 162 MW in Uisenis (Ingram, 2016). According to SSE the current connected and contracted volume including hydro and wave energy on the Outer Hebrides is 412.6 MW and would require an HVDC cable over a 156 km distance to the next substation on the mainland. However, due to the estimated cost of at least £780m and the poor profitability, it is still on the edge (BBC, 2018).

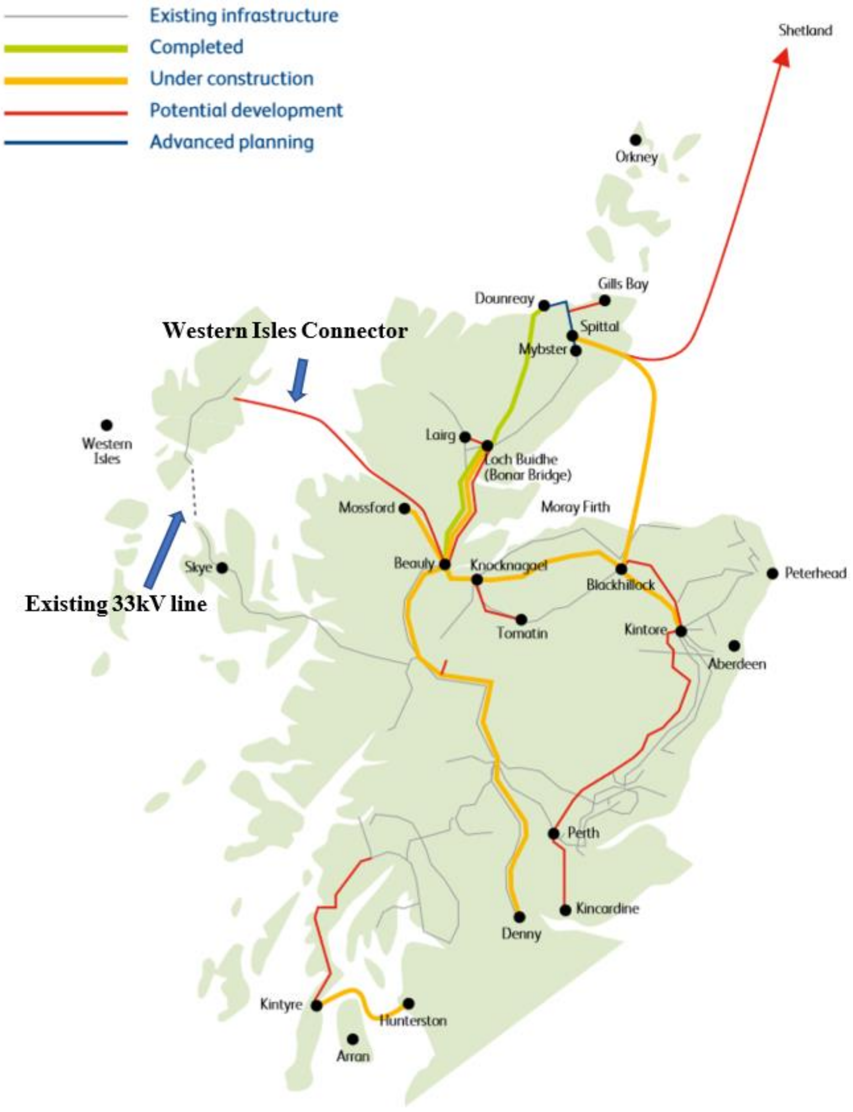


Figure 6: Scottish grid expansion plans (SSE, 2015).

The illustration above also gives an overview of the transmission projects in Scotland. A thin grey line shows the only existing 33 kV connection from the Western Isles to the Isle of Skye which is itself connected by a 275 kV line to the mainland. 33 kV lines are very limited in their capacity and cannot transfer additional power from proposed wind farms on the islands. Therefore, it is mandatory to think about different approaches to export energy which is abundant due to good wind occurrence (Menzel, et al., 2010).

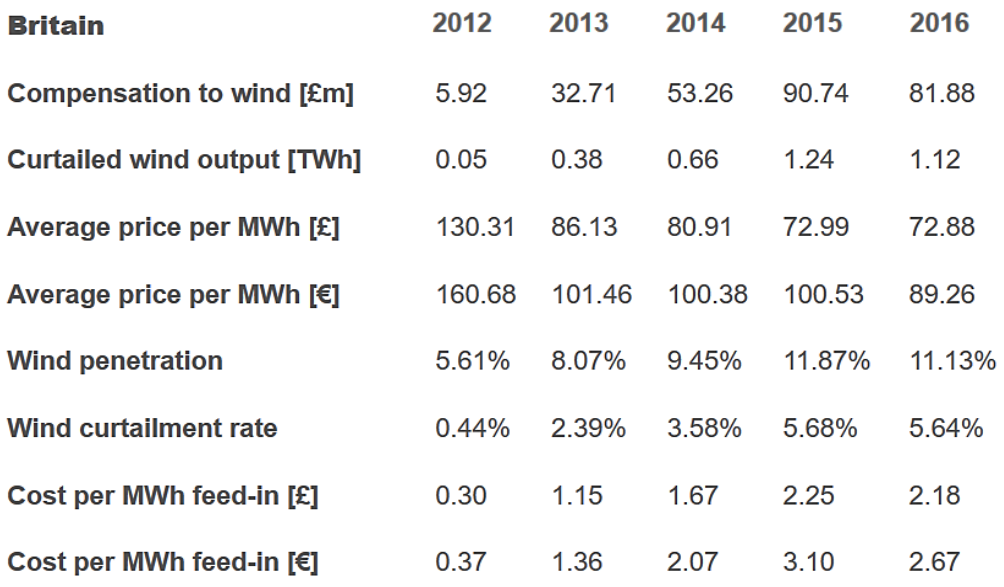
2.1.3. The Issue of Oversupply

Existing power grids were designed to distribute electrical power to people, with the logical consequence that less populated regions have lower grid capacities compared to densely populated areas. However, large wind and solar farms are often located in remote areas far off from large cities and transmission lines become more and more overloaded. In the Southwest of England, one of the essential 132 kV transmission lines has reached its full capacity because of the good conditions for solar energy and massive expansion of photovoltaics over the last few years (Palmer, et al., 2017).

Wind and solar farms receive for their delivered electricity to the grid so called Renewables Obligation Certificates (ROCs) which are worth £40 per MWh (Joos and Staffell, 2018). In case of good wind occurrence or solar radiation leading to a grid overload, the operators of renewable energy must switch off their generation sites to avoid grid instabilities. Therefore, they have compensation contracts and payments for reducing their output. In 2016, the National Grid had to pay about £82m to wind farm operators for switching off their turbines because they were producing more power than the grid could take. According to a National Grid spokesman, it is a measure to avoid grid overload and the cheapest way to manage green energy while reinforcing the electrical network. Nevertheless, in the end, the consumers must pay the bill for this constraint payments. In total, the National Grid has spent £1.6 billion since 2014 switching different energy sources on or off because the grid cannot cope with the power in certain areas (Millard, 2017).

Table 1 shows the drastic increase in wind generation and the related costs of constraint payments. The payments to shut down wind turbines have risen by £22.7m per year over this period or by £5.8m for each TWh generated by wind (Joos and Staffell, 2018).

The quantity of wind curtailment has grown substantially from 45 to 1123 GWh between 2012 and 2016. The curtailment prices per MWh averaging £73 in 2015 and 2016, are well above the ROC buyout and market prices, which are £44–45 per MWh in these years (OFGEM, 2018). It is a conflicting fact, that right now it is more economical for wind farm operators to switch off turbines instead of selling actual energy to the grid.



Britain	**2012**	**2013**	**2014**	**2015**	**2016**
Compensation to wind [£m]	5.92	32.71	53.26	90.74	81.88
Curtailed wind output [TWh]	0.05	0.38	0.66	1.24	1.12
Average price per MWh [£]	130.31	86.13	80.91	72.99	72.88
Average price per MWh [€]	160.68	101.46	100.38	100.53	89.26
Wind penetration	5.61%	8.07%	9.45%	11.87%	11.13%
Wind curtailment rate	0.44%	2.39%	3.58%	5.68%	5.64%
Cost per MWh feed-in [£]	0.30	1.15	1.67	2.25	2.18
Cost per MWh feed-in [€]	0.37	1.36	2.07	3.10	2.67

Table 1: Curtailment rates in Britain (Joos and Staffell, 2018).

The main reason for curtailment is the lacking network capacity between Scotland and England. Therefore, not only the expansion of the electrical network is necessary, but also opportunities to store surplus energy for times of lower generation. Some projects are already in progress to reinforce the grid such as the Western Link subsea connection which is a 600 kV high voltage direct current connection to deliver renewable energy from Scotland to England and Wales (Western Link, 2018).

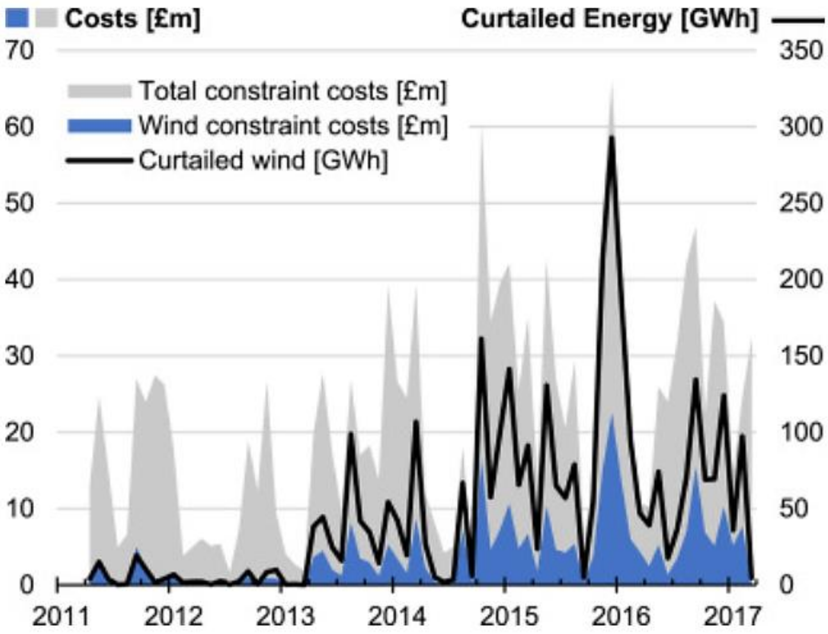


Figure 7: Power fluctuations in relation to curtailed energy (Joos and Staffell, 2018).

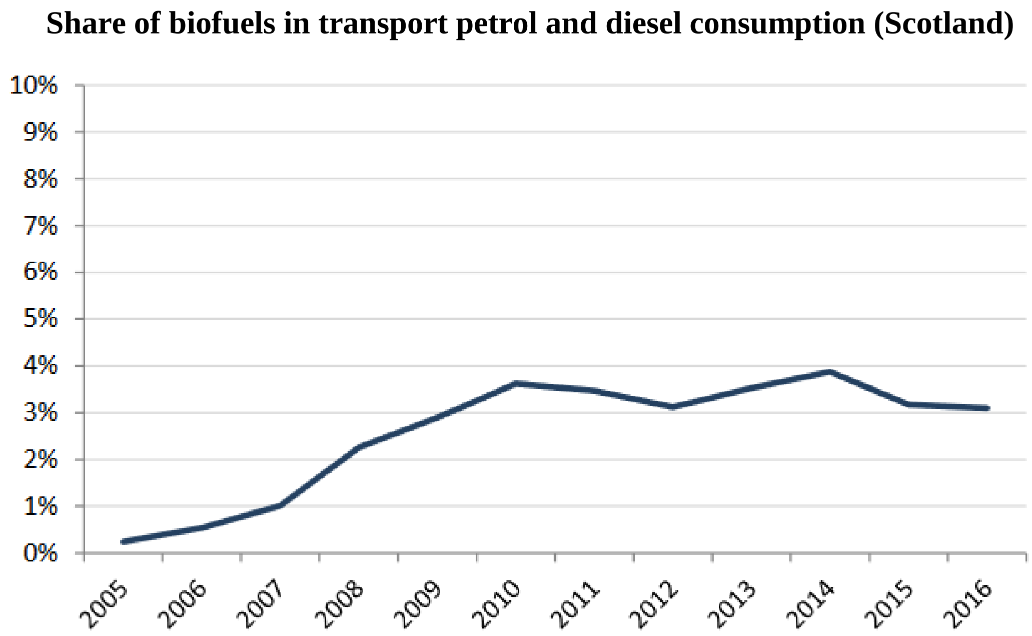
This discussed issue is addressed by the present paper by another approach, i.e. the conversion of excess energy into renewable fuels. This approach is a proposed solution to balance the electrical grid on a large scale and to decarbonise the transport sector at the same time. Harnessing all the surplus wind energy can save millions of pounds of constraint payments, reduce the expansion costs of transmission lines in remote areas and increase the share of renewable energies in the electrical grid as well as in the transport sector.

2.1.4. The Transport Sector

The transport sector amounts for 25% of the total energy use in Scotland. The share of passenger traffic is 60% and the share of goods traffic is 40%. In 2017, only 3% of the consumed transport fuel was based on renewable sources, the target for 2020 was defined with 10% though (Scottish Government, 2018).

Figure 8 shows that the increase in biofuels in road transportation is very humble remaining constant over the last 7 years. However, it does not include a significant rise in electric vehicles which turned out to be more popular than cars using biofuels. In 2016, there were around 7,000 pure electric and 14,000 hybrid electric vehicles on

Scottish roads, which is more than twenty times the amount ten years ago. Future prospects for electric vehicles are controversial but a further increase is doubtless.



Share of biofuels in transport petrol and diesel consumption (Scotland)

Figure 8: Biofuels in Scotland (Scottish Government, 2018).

Whereas rail transport is more and more electrified, the share of biofuels in the marine and aviation industry is vanishingly low. One of the issues of applying biofuels in shipping is the amount of fuel needed i.e. a single very large carrier consumes around 100 million litres a year (Hsieh and Felby, 2017). Currently, renewable diesel-type fuels are produced by plant-based oils but the required area for growing the bio-feedstock for a shift towards biodiesel in the entire shipping sector has serious environmental impacts.

The merchant shipping sector consumes more than 330Mt of fuel a year and accounts for 2-3% of the global CO2 emissions, 4-9% of SOx emissions and 10-15% of NOx emissions (*ibid*). More than 85,000 vessels are registered with a share of 20% medium and large-scale vessels accounting for 80% of the total gross tonnage *(ibid).* These ships primarily use Heavy Fuel Oil (HFO) or Marine Diesel Oil (MDO) with a high viscosity and high sulphur level, having severe effects on water and air pollution (*ibid*).

The shipping industry has been excluded from the Paris Agreement because it involves international activities and cannot be affected by any national regulations. Regulations can only be determined by the International Maritime Organisation (IMO) constituted by over 100 countries. Some of these countries, such as Argentina, Brazil or Panama are against limits on emissions (Shukman, 2018). Nevertheless, some coastal waters in Europe and North America have set up Emission Control Areas (ECAs) with limits on sulphur content in fuels, i.e. only fuels with a sulphur content below 0.1% are allowed in this area. Regulations on CO2 emissions have not been determined yet (Hsieh and Felby, 2017).

Nevertheless, due to more efficient ship engines, CO2 emissions of shipping have been reduced by 47% in Scotland between 1990 and 2015 (Transport Government Scotland, 2017). Synthetic fuels produced by renewable electricity have not been considered so far, but they might be a good alternative, if not the better path, towards a sustainable and carbon-free shipping industry.

2.2. Overview of renewable fuels

Synthetically produced fuels by using renewable electricity are not only possible successors of fossil fuels but can also establish a new segment in the energy market, filling a gap between non-dispatchable power generation and increasing energy demand. As already discussed, the transport sector needs energy dense, reliable and easily transportable fuels without dramatic changes in infrastructure and reasonable costs to produce in large quantities. These strict requirements are responsible for the slow progression of such fuels. As soon as renewable fuels get cost-competitive the shift won’t last long. Advantages of low carbon emissions or even carbon-free emissions, their abundance and decreasing production costs support the development of such fuels. Increasing oversupply of electricity generation through renewable resources provide cheap energy for conversion processes to be competitive. Figure 9 shows that the resources for the production and the emissions from renewable fuels close within a cycle. The conventional carbon cycle also closes itself, but the time for the natural conversion of carbon emissions into fossil fuels takes millions of years and is not in balance with the daily amount of emissions we produce. The following chapters describe some of the most promising renewable fuels in more detail.

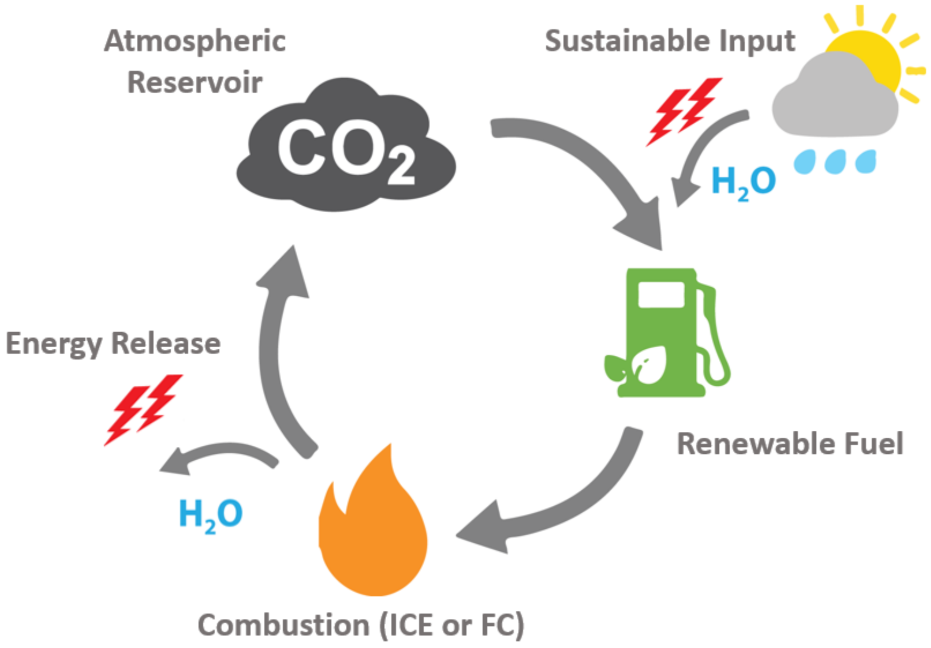


Figure 9: Life cycle of renewable fuels (Source: Own design, adapted from DIFFER, 2018)

2.2.1. Hydrogen (H2)

Pure hydrogen is the most energy dense fuel on a gravimetric basis with 142 MJ/kg high heating value, which is more than double the amount of petrol or diesel (Gray, 2007). However, on the volumetric basis, one litre of liquid hydrogen only contains around 8 MJ which is about a quarter of petrol (*ibid*). It is also very expensive and energy intensive to store and distribute pure hydrogen in a liquid state. A more affordable approach storing hydrogen in a gaseous state at 350bar has an even lower volumetric energy density of 3 MJ/litre (*ibid*).

Production

The most common technology for hydrogen production is still steam reforming of fossil fuels such as natural gas. It consumes lots of energy, is costly and releases carbon monoxide, or in case of an additional shift conversion, the slightly less harmful CO2. Due to high emissions and fluctuating natural gas prices, the path towards a more sustainable and independent production of hydrogen has been initiated.

One of the most promising technologies is the water electrolysis. It is a simple electrochemical process splitting water by electricity to produce hydrogen and oxygen as reaction products. The positively charged anode and the negatively charged cathode are separated by a solid membrane material i.e. the most commonly used is a proton-exchange membrane (PEM) made of a special plastic. At the anode, water reacts to oxygen and hydrogen ions. The positively charged hydrogen ions move through the membrane to the cathode, where they react with electrons to hydrogen gas.

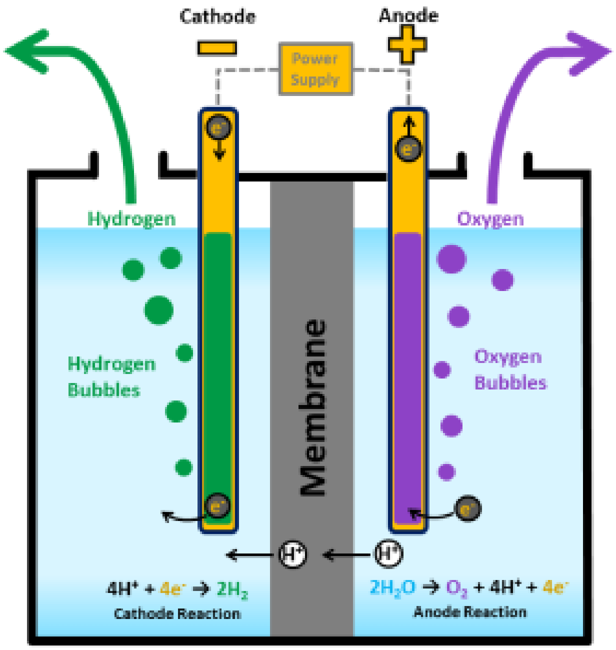


Figure 10: Schematic of water electrolysis (U.S. Department of Energy, 2018).

Efficiency

The work requirement of splitting water within large electrolyser units is between 55-65 kWh/kg per produced hydrogen gas, depending on the utilization of the excess heat and the electrolyser type (ITM Power, 2017). The stack efficiency of recent electrolyser modules operating under 80 bar reach up to 77% without heat recovery and 86% with heat recovery systems (*ibid*).

Hydrogen is the lightest of all gases with extraordinary properties which do not meet the requirements of the market, especially in the transport sector. In terms of the feed-stock, the only resources required are water and electricity which makes hydrogen the cleanest fuel of all with the least environmental impact. Not only the production by electrolysis but also the storage and distribution of the gas is expensive, energy consuming and technically challenging.

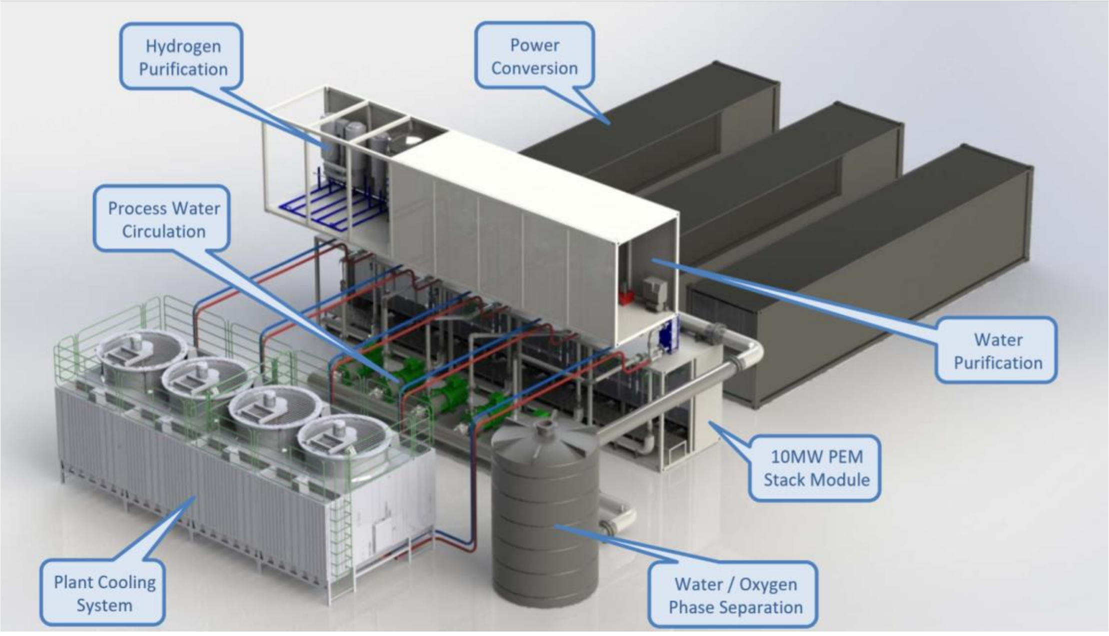


Figure 11: Hydrogen production plant (ITM Power, 2017).

Storage

The potential to store hydrogen at an appropriate energy density is one of the largest issues. The work requirement for the compression of hydrogen gas is considerable and amount to 2.2 kWh/kg for isothermal compression from 20 bar to 350 bar (Gardiner, 2009). The energy required to reach 700 bar including precooling for a better volumetric energy density amounts to 3.2 kWh/kg (*ibid*). Liquefaction to the cryogenic state at 20 K is the most energy dense form to store hydrogen and requires at least 7 kWh per kg produced hydrogen (Valenti, 2016). All this energy required for storing hydrogen is at the cost of efficiency but also presupposes sophisticated tanks with strict safety precautions.

Many car manufacturers have avoided a serious move towards hydrogen yet, not only because of a low energy density per volume but also because of infrastructure and storage issues. Tesla CEO Elon Musk even describes the idea of using hydrogen in cars as ‘incredibly dumb’ (Muoio, 2016).

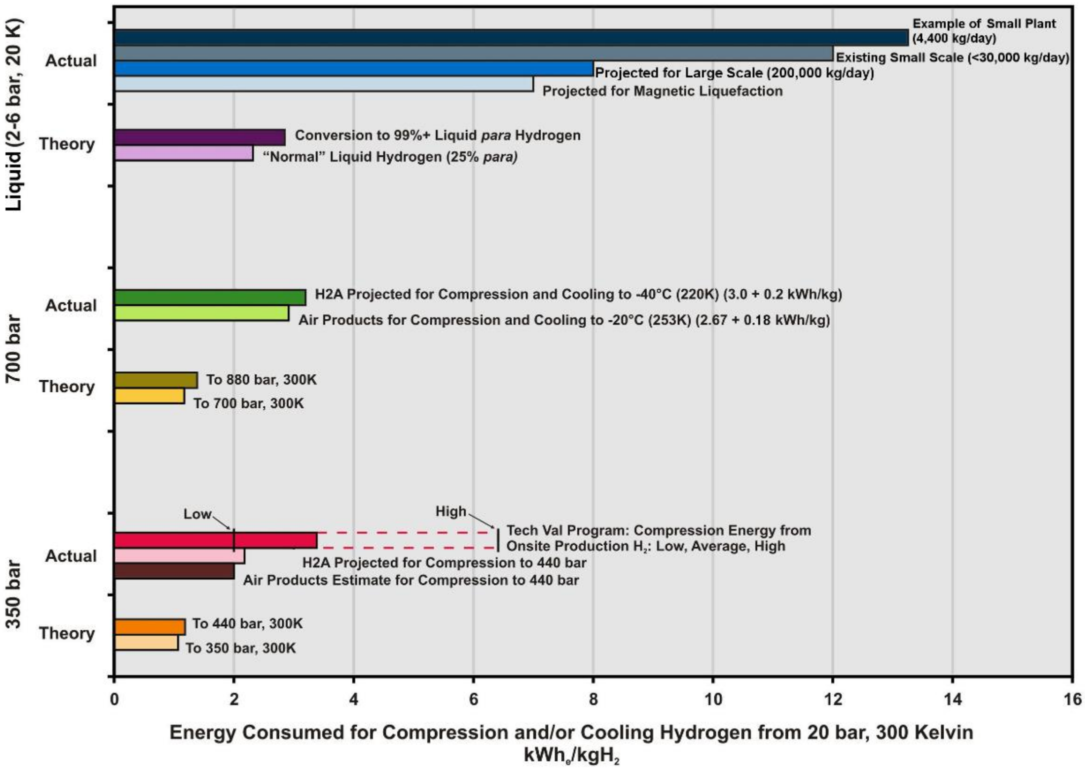


Figure 12: Work requirement for hydrogen compression/liquefaction (Gardiner, 2009).

Environmental impacts and safety issues

Hydrogen is an odourless, colourless and the most abundant element in the universe. It is rarely found in its pure diatomic form but usually in a wide variety of inorganic and organic chemical compounds, the most common being water (H2O). The combination with carbon is essential for organic life and important for the formation of sugar, fat and proteins (Hirscher, 2010). However, in its pure form, it is considered as an indirect GHG through its reaction with hydroxyl (OH) radicals, which increases the lifetime of the direct GHGs methane and ozone (Derwent, et al., 2006). The leakages of pure hydrogen though, are expected to be negligible and the impact to the atmosphere likewise.

In terms of safety, the handling with hydrogen needs to be done cautiously. The reactivity of hydrogen at room temperature is very low. However, at higher temperatures, the mixture with chlorine or oxygen leads to very explosive reactions. Especially the mixture of hydrogen and oxygen in a 2:1 ratio is highly explosive, known under the name laughing gas (Britannica, 2018). The energy to start a hydrogen/oxygen explosion is very low and even small sparks are fatal. Nevertheless, since hydrogen disappears quickly from any leakages the risk is vanishingly low and the handling of hydrogen quite safe and ecologically harmless.

After all, hydrogen is a very interesting substance with many advantages for specific appliances, but it might not be the best solution for land, sea or air vehicles with the contradicting requirements discussed. Therefore, alternative synthetic fuels which are based on hydrogen or consist to a large extent of hydrogen should be closely investigated.

2.2.2. Ammonia (NH3)

Ammonia is known as a fertiliser or coolant but hardly as an energy carrier. However, it is the best hydrogen carrier with 18% of its mass being hydrogen, which is 136 kg per m³ (Bossel and Eliasson, 2003). This amount is around double the number of pure liquid hydrogen because latter has a lower volumetric energy density. Although the heating value of ammonia is with 22.5 MJ/kg only half of petrol or diesel, the volumetric density of 13.6 MJ per litre is among the highest of non-conventional fuels (Zamfirescu and Dincer, 2009). Figure 13 shows an interesting list of fuels with hydrogen contents and volumetric energy densities. Interestingly all containing more hydrogen and more energy per cubic meter than hydrogen in its pure form. Furthermore, ammonia does not contain any carbon atoms and is beside hydrogen the only carbon-free substance with great potential as a fuel. Thus, there is no formation of carbon emissions or particles during combustion (Thomas and Parks, 2006).

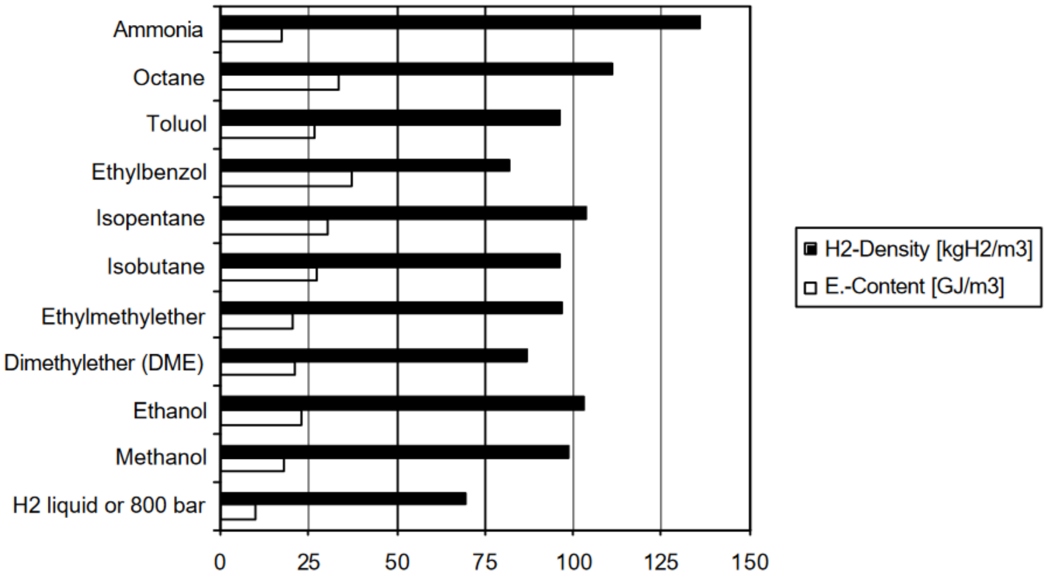


Figure 13: Hydrogen content of different fuels (Bossel and Eliasson, 2003).

Another big advantage is that ammonia can be stored in a liquid state at 25°C and moderate 10bar in standard steel tanks which are already used for liquefied petroleum gas (Hahn, 2018, Engineering Toolbox, 2011). Furthermore, ammonia has been already used for a century as a refrigerant or in the fertilizer industry, and is one of the most produced chemicals in the world with an annual production of 170 million metric tons (Brown, 2016). In other words, the industry knows very well how to deal with ammonia and the necessary infrastructure is available. Experience has shown that there is no great disadvantage regarding toxicity compared to fossil fuels. Even if there occur leakages, dissipation occurs quickly, due to its lower density than air. Only people in the immediate surrounding are affected (Thomas and Parks, 2006). Its narrow flammability limits of 16-25% by volume in air, imply low explosion danger and safety in handling (Zamfirescu and Dincer, 2009).

Production

The production of ammonia is primarily done by ammonia synthesis or also called Haber-Bosch process. The process was invented by the German chemist Fritz Haber in 1909 and further developed to an industrial process by Carl Bosch (Britannica, 2016). Until now, the fertilizer industry uses this process with natural gas as a hydrogen resource to produce large quantities at affordable costs. To make the process sustainable, hydrogen can be produced by renewable electricity through water electrolysis. Figure 14 shows the overall process of ammonia production and all the necessary ancillary processes. Main constituents for the processes are water, which needs to be purified in a mechanical vapour compressor (MVC), and air, which needs to be separated into nitrogen, oxygen and other elements. Eventually, electricity provides the energy input to the system. After all, just three abundant resources are required to produce a universal applicable fuel with an appreciable energy density and properties enabling a convenient storage and distribution.

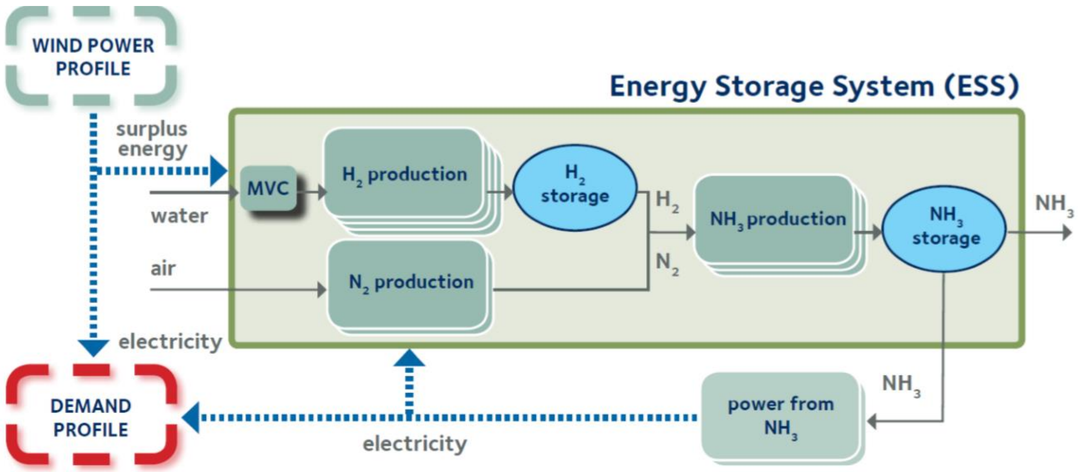


Figure 14: Example of an ammonia energy storage concept (Banares-Alcantara, et al., 2015).

Having a closer look at the synthesis process (see Figure 15), it must be mentioned that it is a recycling process meaning that the conversion into ammonia is only about 15% each pass but by continuing recycling, within the reactor, a conversion of 98% can be reached (Clark, 2013). The mixture of hydrogen and nitrogen going into the synthesis reactor is in the ratio of 3 hydrogen molecules to 1 nitrogen molecule. The hydrogen can be produced by water electrolysis but must be of high quality to avoid poisoning the catalyst. Nitrogen is abundant in the air and can be extracted by air distillation or by the more efficient pressure swing adsorption.

$$N_2 + 3H_2 \xrightarrow{yields} NH_3(\Delta H = -92.44 \frac{kJ}{mol})$$

Equation 1: Ammonia synthesis

The ammonia synthesis is an exothermic reaction, releasing around 2.7 GJ of heat per metric ton of ammonia produced (Morgan, 2013). Standard reaction conditions are pressures ranging from 200 bar to 400 bar at temperatures between 400°C to 600°C (Thomas and Parks, 2006). The iron-based catalyst is one of the crucial components and different materials have been researched to achieve a good speed of conversion. To minimise the heat losses a heat exchanger reheats the recycled gas before entering the reactor again. Eventually, a condenser is needed to liquify the ammonia and to split it from the unreacted hydrogen and nitrogen (Clark, 2013).

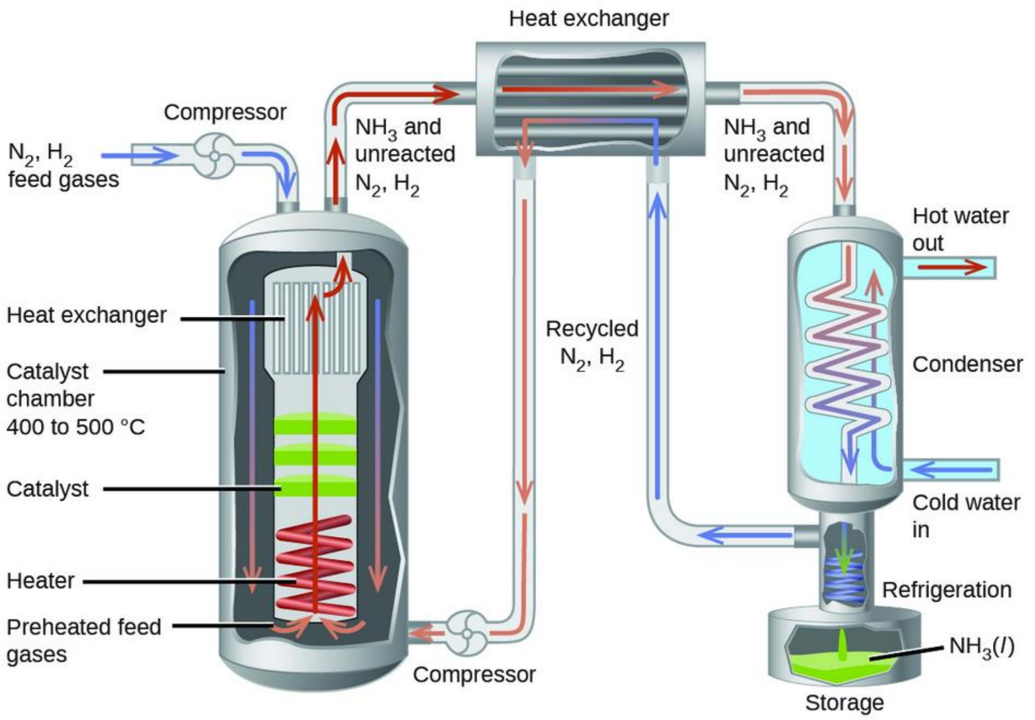


Figure 15: Haber-Bosch process (British Columbia Campus, 2017).

Efficiency

The Haber-Bosch process itself does not require energy since it is an exothermic process. However, to provide hydrogen and nitrogen, either the fossil-fuel based steam reformation or the sustainable, but energy intense electrolysis, consuming around 11 MWh per metric ton of ammonia produced, are essential (Morgan, 2013). The separation of air into nitrogen and oxygen by pressure swing adsorption consumes around 0.09 MWh/t (*ibid*). There is also some energy required for the compression and recycle pumps, which amounts to 0.64 MWh/ton of produced ammonia. Almost negligible but still considered is the energy for the purification of water in the mechanical vapour compression (MVC) process. Morgan's model says that the overall electrical energy consumption including the electrolysis amounts to 11.6 MWh per ton of ammonia. Figure 16 shows the share of power consumption by process component, with the obviously largest consumer being the electrolyser responsible for more than 93% of the entire ammonia production. It also underpins that the synthesis of hydrogen and nitrogen to ammonia is efficient and attractive compared to the energy required for compression and liquefication of hydrogen for storage purposes. Further detailed comparison of the ammonia production processes is conducted in Chapter 4.2.

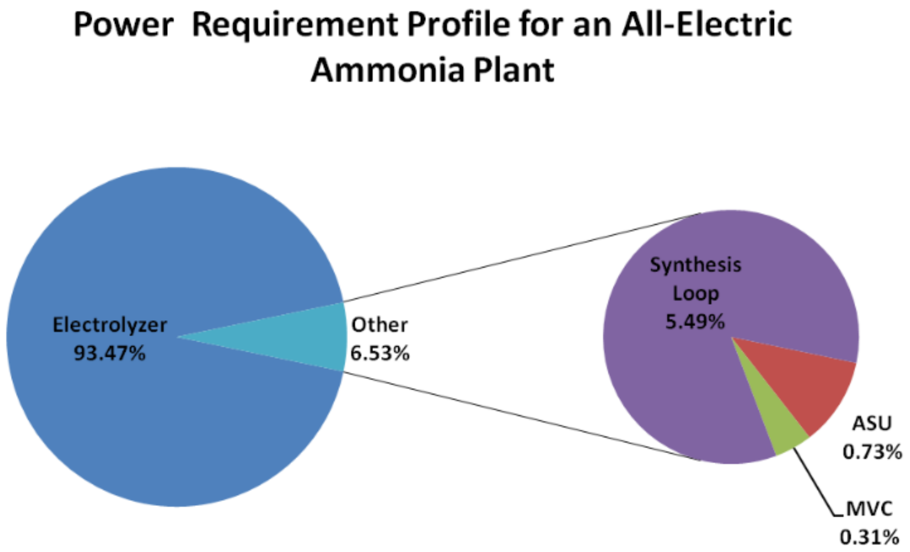


Figure 16: Power requirements for ammonia production processes (Morgan, 2013).

Environmental impact and health issues

Ammonia is a colourless, highly irritating gas with a pungent, suffocating odour (NY State Department of Health, 2004). In high concentration, it is a toxic substance for humans and the environment. However, ammonia is part of the life-essential nitrogen cycle. Nitrifying bacteria enables the fixation of the unreactive nitrogen into nitrates which are needed to form proteins (Bernhard, 2010). Naturally, ammonia occurs in lightning strikes and in a larger scale in bacteria, decomposing plant waste and animal or human excrements. In the air, it forms the non-toxic ammonium (NH4+), which is converted into essential nitrates after rainfall and used by plants as a natural fertilizer (Minnesota Department of Agriculture, 2018). Elevated concentrations in water or atmosphere can harm organisms including animals and humans but also aquacultures. It is easily detectable for humans at very low levels of 5ppm and immediately fatal from 10,000ppm or 1% concentration in air by volume. Above 400ppm, human feel severe irritations of eyes, nose, ears and throat but without lasting effects on short exposure (Thomas and Parks, 2006). However, also other fuels like petrol or diesel are toxic having even similar or even worse impacts on the environment. In terms of safety, it is classified as a non-flammable gas because it has narrow flammability limits of 16-25% by volume in air (Afif, et al., 2016).

As already mentioned requirements for the distribution of ammonia would be very similar to liquefied propane gas (LPG), hence existing trucks and ships can be used with only minor additional safety features. Ammonia is considered as one of the best hydrogen carriers that can be produced at a reasonable price, transported efficiently and transformed directly to yield hydrogen.

2.2.3. Methanol (CH3OH)

Methanol is considered as one of the most attractive alternative fuels to petrol and diesel. It has the highest hydrogen to carbon ratio of all hydrocarbons with only 38% of its mass being carbon (Andersson and Salazar, 2015). Methanol can be produced from a wide variety of fossil or renewable feed-stocks and is plentiful in the industry with about 70 million tons of annual production (*ibid*). It is one of the most handled chemicals worldwide used for many purposes in the chemical industry but also as blend in petrol. Its availability is given in almost every large port around the globe and existing storage tanks for fossil fuels can be used to store methanol as well.

The physical properties are comparable to other marine fuels and storage would only require minor modifications, since it remains as a liquid at ambient temperature and pressure. The energy density or higher heating value is approximately 22.9 MJ/kg on a gravimetric basis and 18 MJ/litre on a volumetric basis, which is a bit less than a half of the value for petrol or diesel (Olah, 2011). A high octane rate and a high vaporization heat make methanol suitable for high compression ratio engines with large power outputs, meeting the requirements of ship engines (Zhen and Wang, 2015). Only minor engine modifications are necessary to enable methanol being combusted in conventional diesel engines.

One of the few alternative fuel concepts for ships in the multi-megawatt class has been put into practice by the world leading ferry operator Stena Line with methanol. The retrofitting of the 24MW ROPAX ferry Stena Germanica has been successful and is now able to run on both diesel and methanol fuel (Andersson and Salazar, 2015).

Production

Almost any energy resource can be used to produce methanol, but natural gas is with more than 75% share still the most common feedstock (Cifre and Badr, 2007). For brevity of this paper, only methanol production from biomass is considered. Even though electrolytic hydrogen in combination with a carbon source can be also a sustainable approach for methanol production, it is not taken into consideration due to the complexity of the carbon sequestration and a rather bad energy balance with high production costs (Cifre and Badr, 2007).

The processes required for the conversion of biomass into methanol is similar to that of natural gas (see Figure 17). First of all, the biomass feedstock must be dried to a maximum moisture content of 20% (Marine Methanol, 2018). Then, the biomass is pyrolyzed in an oxygen deficient environment under 400-600°C (*ibid*). In this process, the feedstock is thermally composed into biochar and syngas. Before the syngas can be used for the methanol synthesis it needs to be purified from tar, particles and other unwanted gases. The reformer consists of catalysts which split hydrocarbons into carbon monoxide and hydrogen, which are the crucial components for the synthesis. In order to reach the required H2/CO ratio of 2:1, some hydrogen needs to be added to the syngas, which can be recovered from the purge stream of the methanol (Morandin and Harvey, 2015). Eventually, the fresh syngas goes in a loop through the synthesis reactor to reach a good conversion rate and the optimal gas quality. Only around one third in volume of the synthesis loop is added as fresh syngas. The methanol contained in the syngas is separated by cooling and flashing. The final separation also includes distillation and purification of methanol.

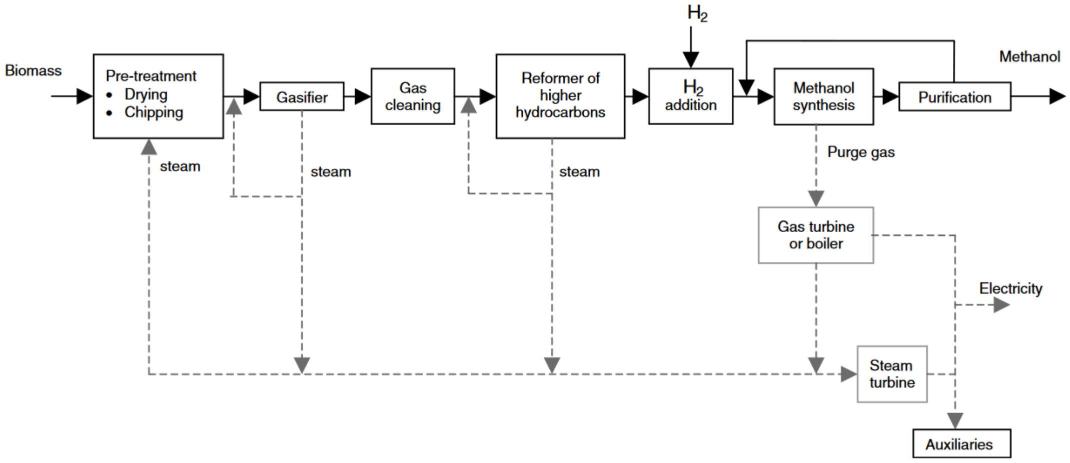


Figure 17: Methanol production process chain (Cifre and Badr, 2007).

Efficiency

There are lots of different designs for methanol production from biomass with different efficiencies depending not only on the design but also on the size of the plant and the feedstock. Most of the literature indicates an overall efficiency from biomass energy content to methanol energy content between 50-60% (Bromberg and Cheng, 2010). The gasification efficiency from biomass to syngas is usually around 80% and the synthesis conversion efficiency of around 70% (*ibid*). In a specific case study carried out by the Chalmers University of Technology in Sweden, the syngas production requires 11.16 MJ/kg and achieves a conversion efficiency of 82.4% (Morandin and Harvey, 2015). The study assumes an oxygen-steam blown pressurised gasifier using wood chips with a higher heating value of 10.43 MJ/kg and a biomass input of 549MW. (*ibid*). The methanol production yields 1285 tons per day which is equivalent to 337 MW. According to their model, the overall conversion efficiency from biomass to methanol amounts 50.8% without heat recovery (*ibid*). These values are used for calculations in the present study.

Environmental impact and safety issues

Methanol is toxic and fatal if taken by humans or animals. However, it is biodegradable and water soluble with the ability of most micro-organisms to oxidize it. Moreover, spills do not have such environmental impacts as HFO (Andersson and Salazar, 2015). Under sunlight, methanol can be rapidly broken down into its compounds and has a half-life of just seven days (Zhen and Wang, 2015). In terms of emissions methanol has significant advantages, only producing 10% of the soot compared to diesel, meeting the Tier II regulations for nitrogen oxide (2-4 g/kWh) and producing no sulphur-oxide emissions at all (Andersson and Salazar, 2015). However, there are CO2 emissions which need to be investigated including the production process. According to Urja (2013), methanol production in Germany based on forest residues would emit 0.56 kg CO2 equivalents per kilogram produced methanol, which could reduce GHG emissions by 24-33 % compared to methanol from natural gas (Urja, 2013).

Concerning safety, one of the most important facts about methanol is that it has a low flashpoint of 11°C, meaning that it can vaporize and mix with air to form a flammable mixture at relatively low temperatures (*ibid*). The flashpoint of HFO is 60°C (*ibid*). Methanol has been used in racing sport also because of its lower safety concerns, due to its characteristics of harder ignition, less radiant heat and easier water quenching ability (Bromberg and Cheng, 2010). Safety requirements are necessary, but in many ways, it is similar to the safety precautions of conventional fossil fuels.

In general, it can be said that compared to gasoline or diesel fuel, methanol is safer and more environmentally acceptable. In countries with large abundance of feed-stocks for methanol production such as China, the popularity and importance is way higher with a share of 17% of all vehicles fuelled by methanol in 2013 (Andersson and Salazar, 2015). Furthermore, it has become a popular choice for the development of fuel cell technologies, especially direct methanol fuel cells (DMFCs).

2.2.4. Other Potential Fuels

Liquid Natural Gas (LNG)

LNG cannot be entirely considered as an alternative fuel since natural gas in its compressed form is widely used in industry or for power generation. However, in transportation, it is not commonly used at all. Even if CO2 and NOx emissions are lower from LNG, combustion compared to conventional marine fuel oil, carbon monoxide and hydrocarbon emissions mainly unburnt methane has severe environmental impacts (SCU, 2016). The main constituent of natural gas both in compressed or in liquefied form is methane which is one of the worst GHGs. In terms of global warming impact, methane is contributing 20-30% more than CO2. Even if the combustion of LNG or compressed natural gas (CNG) does not release any methane, leakages during the production and distribution harm the environment (SCU, 2016).

There are other reasons why LNG could not establish as a mass fuel for transportation. A very practical issue is the storage of LNG due to its boiling point of -161°C. Most of the tanks are cryogenic double-walled steel tanks with a very low pressure of less than 10 kPa. The energy required for keeping the liquid below its boiling point is around 0.85 MWh/ton (Dhameliya and Agrawal, 2016). Costs for these tanks are very high and issues but with a way lower energy density.

A recent study carried out by Wood Mackenzie, says that around 10% of gas processed by an LNG terminal is lost into the atmosphere (Buosso, 2017). Due to these facts and the circumstance that the production of LNG by renewable resources such as biomass is more complex than the production of methanol, it is not considered as a proposed future fuel for shipping.

Dimethyl ether (DME)

DME is the simplest ether with the formula CH3OCH3. It can be produced either by indirect synthetic methods through a dehydration reaction of methanol or in a direct reaction from natural gas (Park and Lee, 2014). DME is colourless, non-toxic, a non-GHG and liquid above 5 bar and ambient temperatures. In terms of emissions, DME is essentially soot-free because of no carbon-to-carbon direct bonds (*ibid*). Emissions of nitrogen oxides and carbon monoxide are very much depending on combustion conditions. DME has a high cetane number from 55 up to 60 with good compressibility. Therefore, it is considered as an alternative fuel for compression ignition engines replacing diesel fuel (Berg, et al., 2013).

Safety issues appear due to its low flashpoint of -41°C which makes it highly flammable. Yet the auto-ignition point is at 350°C and no instant ignition occurs with suitable precautions (ILO and WHO, 2002). Physical properties are similar to liquid petroleum gas (LPG). However, the low density requires large tanks and its low viscosity characteristics cause leakage, which must be prevented by proper additives. Another point of interest is the heating value of 28 MJ/kg, which is significantly lower compared to diesel but slightly higher than methanol (Park and Lee, 2014). The main reasons why this fuel is not further considered are the following. First, its poor lubrication behaviour requires additives and compression of the fuel for a good combustion behaviour. Second, the production is highly complex only using sustainable resources, making methanol more advantageous. Lastly, the lack of experience and low production rates make DME an underdog with higher implementation risks.

3. Application of Renewable Fuels in Shipping

Even if alternative fuels and sustainable production methods emerge, there are still one or more propellers which need to be driven mechanically. For many decades it was the most common method to use marine fuel engines with a direct mechanical propeller shaft drive. The introduction of power electronic devices and converters in the late 20th century, has made it possible to install large electric propulsion drives. Depending on the application, both concepts have their advantages and disadvantages. The following sections deal with both electric ship propulsion systems with energy delivered by fuel cells and internal combustion engines running on renewable fuels.

3.1. Electric Ship Propulsion

The idea of using electric propulsion is not new and goes back to the first diesel-electric ship in 1903 (Pike, 2017). In the cruise ship industry, new-built vessels are already 100% all-electric designs, due to some advantageous characteristics such as room saving, better fuel efficiency and reduced vibrations (Sulligoi, et al., 2016). The purpose of thermal machines on all-electric ships is exclusively driving the shaft of synchronous generators (*ibid*). Especially cruise ships have a high electrical power consumption and can spare a massive generator set which would be required in addition to a conventional engine anyways (*ibid*).

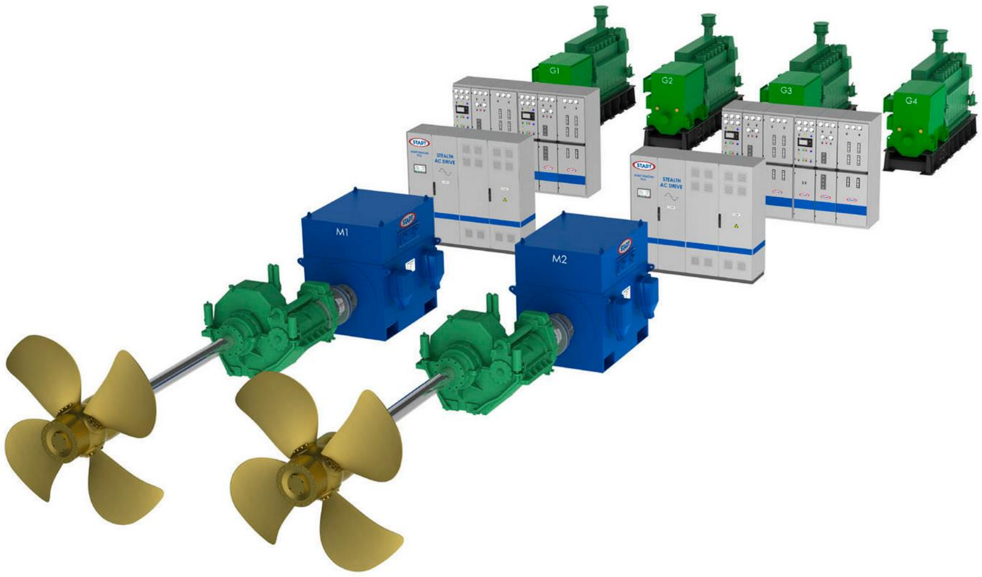


Figure 18: Electric propulsion concept (STADT, 2013).

Figure 18 shows the set-up of a multi-megawatt diesel-electric propulsion unit by the Norwegian manufacturer STADT AS. As shown, the propeller shaft is only connected to the electric motor, which is powered by the electrical output of diesel generators. Power electronics including pulse-width modulation enables a flexible and dynamic control of the electric propulsion unit.

The best efficiency of diesel engines is typically around a load of 85% and the efficiency drops quickly below a load of 50% (Pike, 2017). Thanks to the disconnection of diesel generators and propeller unit, generators can be switched on or off and an optimised operation can be achieved (*ibid*). Especially ferry vessels with shorter route distances compared to ocean-going vessels, cannot run constantly within the optimal load range, resulting in worse efficiency and higher fuel consumption. In terms of reliability, the configuration of several independent generators is very advantageous and even if failures occur the propulsion can be supplied by other generators (*ibid*). The location of units must not be necessarily in the same room since the units are only connected by wires but not mechanically (*ibid*). That brings the advantage of a better use of space. Moreover, noise and vibration emissions are reduced due to shorter drivetrains and smaller generator units (*ibid*).

After all, one of the biggest advantages is the fuel flexibility because the propulsion unit only requires electricity which can be generated either by fuel cells or by any thermal machine which can drive a generator (STADT, 2013).

3.2. Energy Conversion by Fuel Cells

3.2.1. Hydrogen fed Fuel Cells

Fuel cells are the counterpart to the electrolysers. Instead of converting electrical energy into chemical energy, the reaction is in reverse and fuel is converted into electricity. Fuel cells can be also compared with processes of batteries or accumulators with the difference that fuel cells can only release electricity but cannot be charged (Brunet, 2011).

Figure 19 illustrates a polymer electrolyte membrane or **proton exchange membrane fuel cell** (PEMFC) which stands out with high power density, low weight and compact size. The PEMFC works with hydrogen as a reagent, due to its capability to give up electrons by oxidization. The hydrogen first enters the anodic gas diffusion layer and separates at the catalyst surface into protons and electrons. Conventional catalysts are made of nanometre-sized particles of platinum dispersed on a high-surface-area carbon support (U.S. Department of Eneergy, 2017). The protons H+ travel through the membrane or electrolyte to the cathodic layer, while the electrons pass the load and provide electricity. In the cathode the reduction takes place. Oxygen molecules, which have been extracted from the air, react with hydrogen protons and electrons to form water molecules (Abbaspour, et al., 2014).

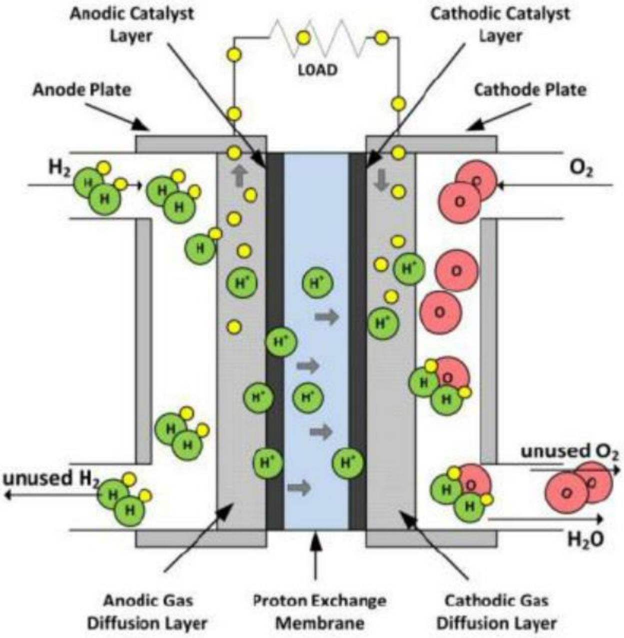


Figure 19: Polymer exchange membrane fuel cell (Abbaspour, et al., 2014).

$\mathrm{H_2} \rightarrow 2\mathrm{H}^+ + 2\mathrm{e}^-$ *Equation 2: Anode reaction (PEMFC)*

$2\mathrm{H}^+ + 2\mathrm{e}^- + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O}$ *Equation 3: Cathode reaction (PEMFC)*

The crucial component is the polymer membrane, which must be a good conductor for protons but at the same time a poor conductor for electrons and other reagents. It requires a temperature of 50-80°C for a satisfying proton conduction (Brunet, 2011). The catalyst allows it to overcome the activation barrier and enhances the reaction kinetics. Best materials are made of noble metals such as platinum or palladium, to persist corrosion and to allow good kinetics even at low activation energy (*ibid*). The reliability and longevity of catalysts are still one of the major issues of fuel cells because any impurities poison the catalyst (*ibid*).

Most of the other fuel cell types are also using hydrogen as a fuel. A common type with many decades of experience in space programmes is the **alkaline fuel cell** (AFC). Instead of using a solid polymer as the electrolyte, an AFC uses a solution of potassium hydroxide in water (Brunet, 2011). Such cells allow a recirculation of the electrolyte, helping to reduce carbonate formation (U.S. Department of Energy, 2017).

$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ *Equation 4: Anode reaction (AFC)*

$\frac{1}{2}O_2 + 2H_2O + 2e^- \rightarrow 2OH^-$ *Equation 5: Cathode reaction (AFC)*

However, this fuel cell type suffers under increased corrosion, wettability and difficulties in handling different pressures, which significantly limits the lifespan compared to the PEMFC (*ibid*). Nevertheless, AFCs can use cheaper and non-precious metal catalysts made of nickel, silver or manganese oxide. Furthermore, they are also less sensitive to poisons and impurities in fuels, giving them an important industrial advantage (Brunet, 2011).

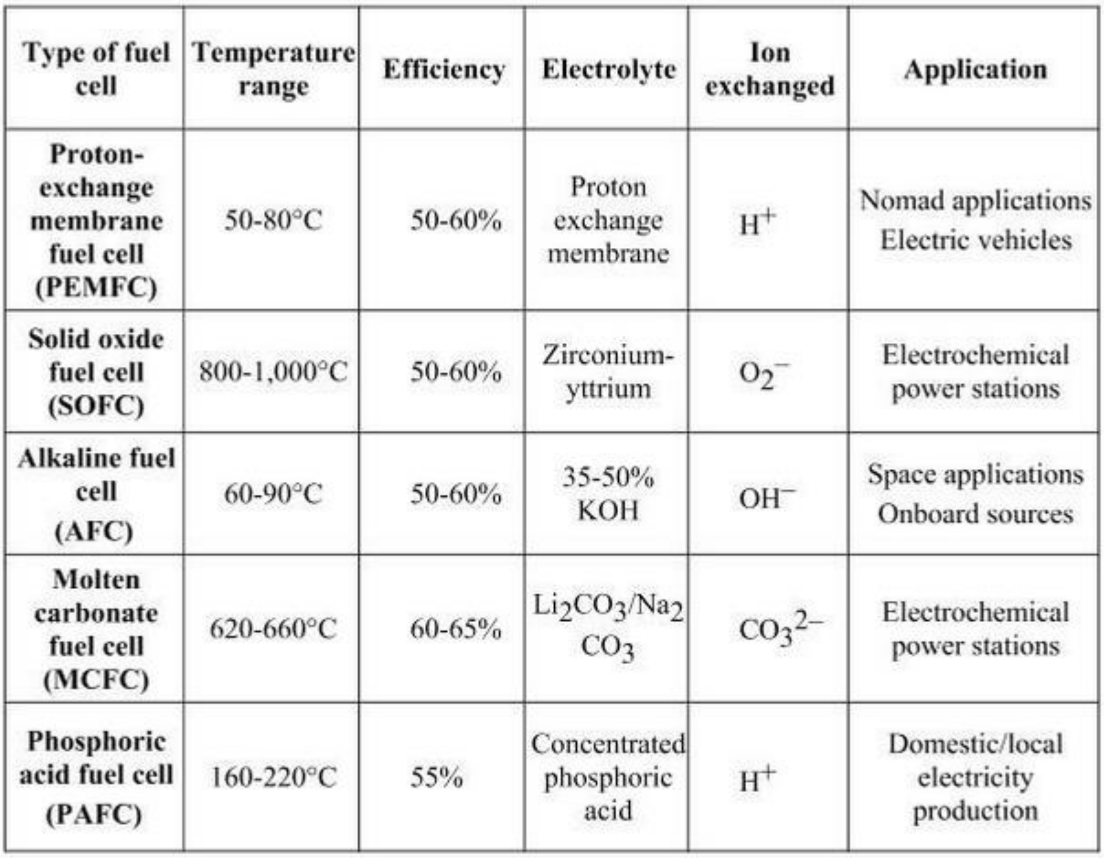
Another common fuel cell type is the **solid oxide fuel cell** (SOFC). This cell works in a different way as oxide ions migrate from the cathode to the anode through the electrolyte (Brunet, 2011). Moreover, the formation of water takes place in the anode or hydrogen part (*ibid*).

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ *Equation 6: Anode reaction (SOFC)*

$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$ *Equation 7: Cathode reaction (SOFC)*

The membranes need to be different and are primarily made of ceramic materials with the correct ionic conductivity and complex compositions (*ibid*). They usually operate between 800-1,000°C, to have sufficient reaction rates (*ibid*). High temperatures eliminate the need for precious-metal catalysts and allow internal fuel reformation, which enables a variety of fuels (U.S. Department of Energy, 2017). Furthermore, they are not susceptible to impurities which is important if another fuel than hydrogen is used (*ibid*). However, high temperatures are challenging in terms of materials and corrosion, especially for the electrolyte, making them unsuitable for fast start and stop applications in transport or for grid balancing purposes due to temperature expansions (*ibid*). The durability of materials under these conditions is also very limited. If waste heat is used for co-generation, the efficiency of SOFCs can be very high, reaching up to 85% (*ibid*). Although there is ongoing research in low-temperature SOFC, satisfying performance has not been achieved so far and materials allowing the reaction at lower temperatures are very rare (*ibid*).

Table 2 gives an overview of different types of fuel cells using hydrogen as a fuel. Even if efficiencies are comparable there are significant differences in operating conditions and materials used as well as in the various fields of application.



Type of fuel cell	Temperature range	Efficiency	Electrolyte	Ion exchanged	Application
Proton-exchange membrane fuel cell (PEMFC)	50-80°C	50-60%	Proton exchange membrane	H^+	Nomad applications Electric vehicles
Solid oxide fuel cell (SOFC)	800-1,000°C	50-60%	Zirconium-yttrium	O_2^-	Electrochemical power stations
Alkaline fuel cell (AFC)	60-90°C	50-60%	35-50% KOH	OH^-	Space applications Onboard sources
Molten carbonate fuel cell (MCFC)	620-660°C	60-65%	Li_2CO_3/Na_2CO_3	CO_3^{2-}	Electrochemical power stations
Phosphoric acid fuel cell (PAFC)	160-220°C	55%	Concentrated phosphoric acid	H^+	Domestic/local electricity production

Table 2: Overview of different types of fuel cells (Brunet, 2011).

Hydrogen consumption and conversion efficiencies for actual purchasable fuel cells can be found in the appendices.

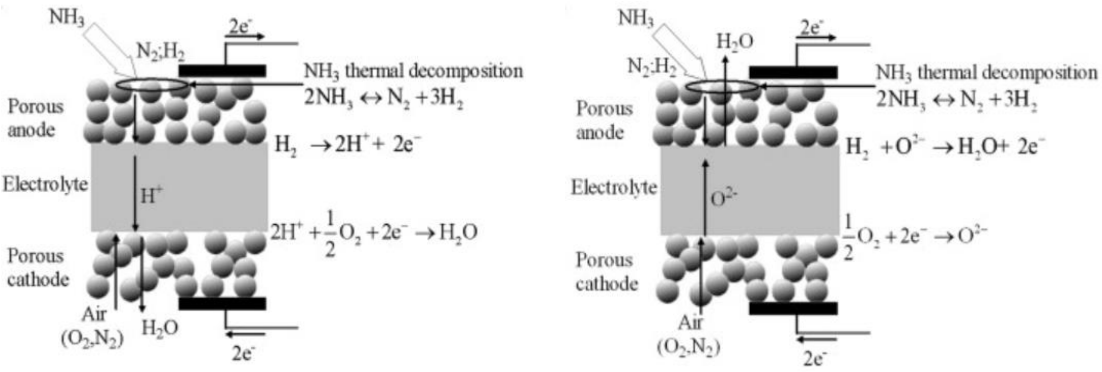
3.2.2. Ammonia fed Fuel Cells

Compared to hydrogen, ammonia is easier to store and to transport. As described in Chapter 2.2.2, ammonia can carry more hydrogen per litre than any other substance including hydrogen itself. Thus, it makes sense to consider ammonia as a fuel for fuel cells. However, most of the fuel cells cannot process nitrogen and ammonia needs to be decomposed or cracked into hydrogen and nitrogen. Compared to the synthesis this is an endothermic reaction meaning that energy needs to put in to achieve satisfying conversion efficiencies. At 600°C and 10 bar a conversion rate of 90% from ammonia into hydrogen can be achieved (Cheddie, 2012). Purification requirements for fuel cells are very strict, especially for PEMFCs. However, high process temperatures also require sophisticated catalyst materials to keep corrosion under control (*ibid*). Thus, it is important to find a good trade-off.

Fortunately, there are also direct ammonia fuel cells emerging. Currently, the best choice appears to be the high-temperature SOFC (Lan and Tao, 2014). As described in Chapter 3.2.1, this type of cell requires high temperatures to reach a good reaction efficiency and decomposition of the fuel. Moreover, high temperatures in combination with nitrogen also lead to the creation of harmful nitrogen oxides which are GHGs and must be avoided (*ibid*). The durability of the anode/electrolyte interface suffers from the local temperature change and redox stable anodes must be improved (*ibid*).

There are two types of ammonia fed SOFC, depending on the characteristics of the electrolyte. They are either hydrogen-proton conducting or oxygen-ion conducting (see Figure 20) (*ibid*). Former appear to be the better solution because of less nitrogen oxide emergence and a higher peak power density (*ibid*). The drawback of more ammonia cross-over must be accepted though (*ibid*).

Same as other fuel cells, the ammonia fed SOFC consists of the three sections namely cathode, electrolyte and anode. Even though ammonia can be used directly as a fuel, it needs to be thermally decomposed to pure hydrogen and nitrogen within the cell (Ni, et al., 2008). In the case of a proton-conducting electrolyte, this happens in the anode at temperatures of at least 500°C (Lan and Tao, 2014).



SOFC-H (H2-proton conducting)

SOFC-O (O2-ion conducting)

Figure 20: SOFC proton and ion conducting schematics (Ni, et al., 2008).

Experiments have shown that the peak power density of proton-conducting electrolytes is 20-30% higher compared to ion-conducting electrolytes with a decomposition in the cathodic layer (*ibid*). Promising catalyst materials are nickel-based composites consisting of nickel and ionic conducting phase (Ni, et al., 2008). The cell efficiency, which was defined as the ratio of electrical work to the heating value of ammonia, can reach up to 72% under ideal conditions of 800°C, a fuel utilization of 80% and an ammonia conversion of 100% (*ibid*). The performance is primarily limited by the transport of hydrogen through the catalyst, as the presence of nitrogen blocks the flow (*ibid*). This results in a lower fuel utilization and lower efficiencies as illustrated in Figure 21.

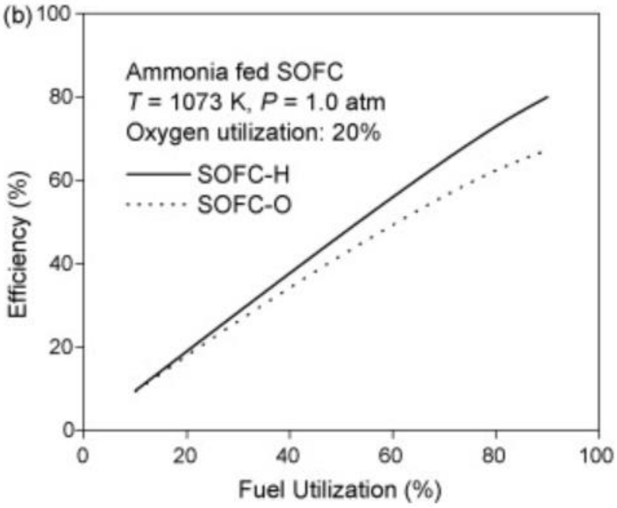


Figure 21: Fuel utilization (Ni, et al., 2008).

The durability of the anode/electrolyte interface is considered as one of the key challenges. It must sustain high temperatures for a good decomposition rate, but it must also avoid the distinct formation of NOx (Lan and Tao, 2014).

When it comes down to it, SOFCs are still in the development stage and many problems need to be solved to achieve commercial success (Lan and Tao, 2014). Nevertheless, with an increasing attention for ammonia as an alternative fuel and cheap electricity for its production, research will get a boost and ammonia fed fuel cells might get competitive to conventional ship propulsion.

3.2.3. Direct Methanol Fuel Cell (DMFC)

Methanol has a great potential as a renewable fuel for shipping and has already shown its success in operation. Even if the combustion of methanol in engines appears to be the obvious solution due to its good fuel properties, it must be acknowledged that direct methanol fuel cells (DMFC) are successful in operation for many applications.

DMFCs are among the most preferred fuel cells for smaller applications up to 5 kW such as portable electrical devices (Samimi and Rahimpour, 2018). This is because of their structural simplicity, high energy density, low pollution and fast operation but also because of their storage easiness and no internal reformation making the system very compact (*ibid*). A low operation temperature and a low excess heat are another advantages, making DMFCs suitable for many applications. The structure is similar to the hydrogen-based PEMFC. At the anode, the oxidation of methanol and water to CO2 and hydrogen takes place (Kamarudin, et al., 2009). Most efficient catalyst materials are platinum or platinum alloys with ruthenium or palladium among others (*ibid*). The electrolyte is a polymer membrane only allowing hydrogen protons to pass through (*ibid*). At the cathode, oxygen molecules reduce with hydrogen protons to form water (*ibid*).

$\mathrm{CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-}$ *Equation 8: Anode reaction (DMFC)*

$\mathrm{\frac{3}{2}O_2 + 6e^- + 6H^+ \rightarrow 3H_2O}$ *Equation 9: Cathode reaction (DMFC)*

One of the main issues in DMFCs is the methanol crossover through the membrane, which significantly reduces the conversion efficiency (Samimi and Rahimpour, 2018). This problem can be diminished by a thicker membrane and more active catalysts, both cost drivers and unfavourable to space requirements (*ibid*). Methanol must be diluted with water in a ratio of approximately 1:1 to achieve good oxidation at the anode (*ibid*). However, this reduces the energy density of the fuel mixture resulting in low performance. The durability of DMFCs suffers under the impact of impurities in methanol, resulting in a poisoned membrane layer (*ibid*). Furthermore, the anode reaction releases CO2 into the environment and may block the pores of the anode layer, decreasing the cell performance even more. Nevertheless, compared to diesel engines, the carbon emissions are vanishingly low.

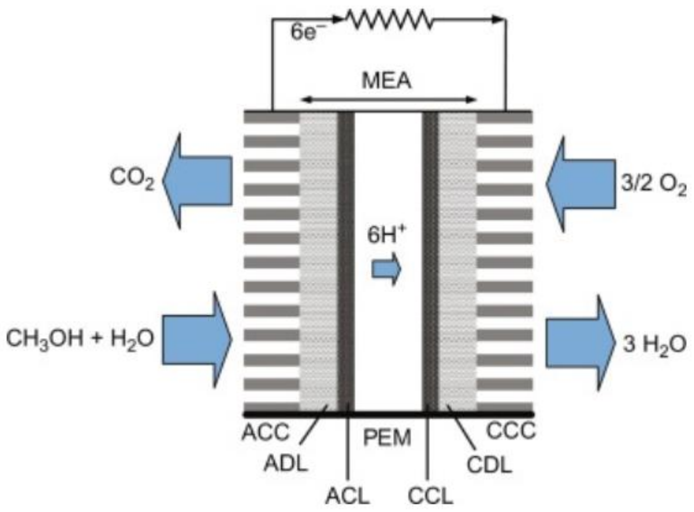


Figure 22: Direct methanol fuel cell (Samimi and Rahimpour, 2018).

There are many purchasable DMFCs on the market, often used for military or civil low power applications in remote areas without access to electricity. According to the Danish fuel cell manufacturer SerEnergy, the silent operation and lower emissions compared to diesel generators are some of the crucial points for its success in specific fields like critical backup power, wireless base stations, secure communication networks or auxiliary power units (SerEnergy, 2018).

3.3. Application in Internal Combustion Engines

3.3.1. Hydrogen

Hydrogen has extraordinary properties and is the cleanest fuel with the best gravimetric energy density. Although most of the research copes with hydrogen for fuel cells, it can be also burnt in an internal combustion engine. The primary combustion product from the reaction with air is water and no carbon emissions. The only GHGs which might occur at high combustion temperatures are nitrogen oxides (Gandhi, 2015). The further bullet points should give an overview of the characteristics of hydrogen as a fuel in combustion engines.

Wide range of flammability

Hydrogen can be combusted over a wide range of fuel-air mixtures enabling also lean mixtures, i.e. the amount of fuel can be below the stoichiometric ideal mixture of fuel and air. The combustion is then more complete, with a higher fuel economy, a lower temperature and less nitrogen oxide formation (Gandhi, 2015).

Low ignition energy

The ignition energy is needed to start the fuel/air mixture reaction. The minimum energy required at 30% hydrogen in air is around 0.02 mJ (see Figure 23). This is more than one order lower than the minimum ignition energy for petrol (0.24 mJ), which has the advantage of prompt ignition and smaller spark plugs. However, this also carries the risk of premature ignition prior to the spark plug, resulting in a rough running engine and efficiency losses (Gandhi, 2015).

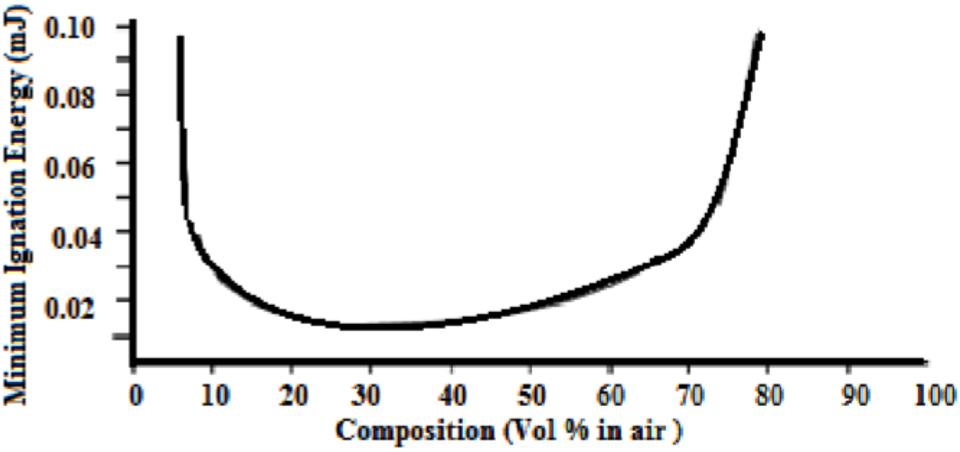


Figure 23: Ignition energy for hydrogen (Gandhi, 2015).

Small quenching distance

It is more difficult to extinguish the flame of a hydrogen-air mixture with the risk of backfiring through the intake valve (Gandhi, 2015).

High autoignition temperature

One of the most important properties for determining the correct compression ratio is the temperature of autoignition. It is at 585°C which is among the highest of all fuels. During compression in the combustion chamber, temperature rises. Hence, a higher autoignition temperature allows higher compression ratios and better thermal efficiencies compared to hydrocarbon fuels. At the same time, it gets more difficult to ignite a hydrogen-air mixture just by compression, i.e. hydrogen engines are, primarily, spark ignition engines (Gandhi, 2015).

High flame speed at stoichiometric ratios

The flame speed is an important key figure for the engine operation and control with impacts on thermal efficiency and emissions. A fast flame speed allows high efficiencies due to a closer operation at the ideal Carnot cycle (Gandhi, 2015).

High diffusivity

A high diffusivity enables a uniform mixture of fuel and air. Furthermore, if any leakages occur hydrogen disappears quickly and fire or even explosion hazards can be minimized.

Air/fuel ratio

Due to the low density of hydrogen, it is difficult to achieve a high energy density in the air/fuel mixture, which reduces the power output. At stoichiometric conditions, hydrogen occupies around 30% of the combustion chamber compared to 1-2% for petrol. However, experiments show that high compression direct injection has a 20% higher stoichiometric heat of combustion per standard kilogram of air compared to petrol. At stoichiometric conditions though, the formation of NOx increases significantly (Gandhi, 2015).

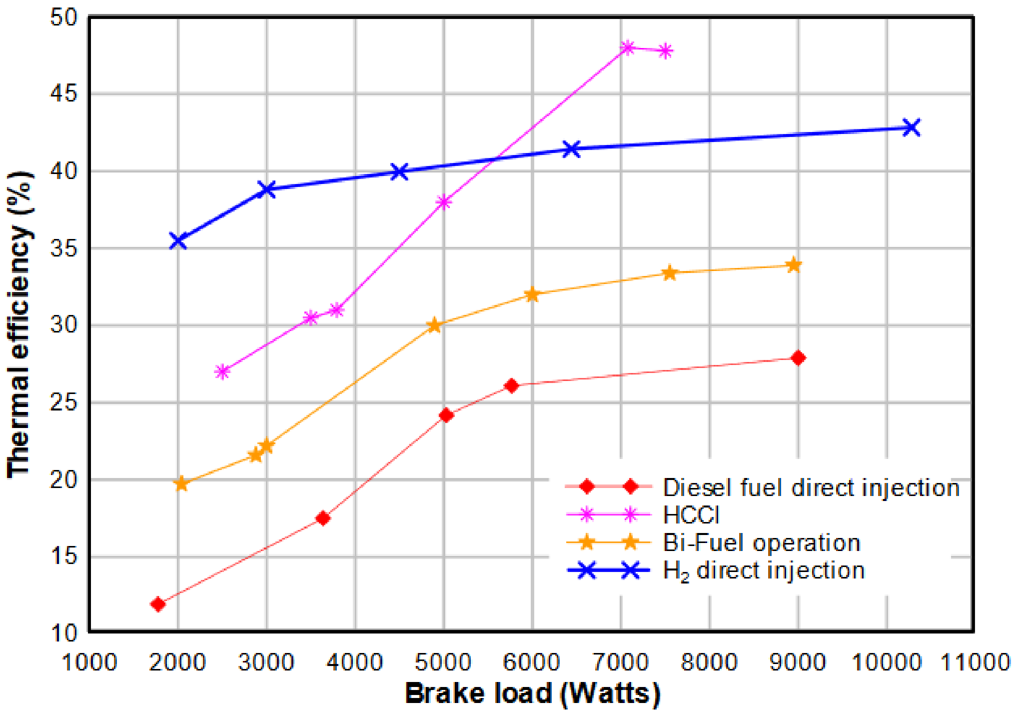


Figure 24: Thermal efficiencies of hydrogen engine (Antunes, 2010).

Another study carried out by Antunes (2010), shows that diesel engines operated on hydrogen can achieve a significantly better thermal efficiency of 42.8% compared to 27.9% for the same engine running on diesel (see Figure 24). Even if the homogeneous charge compression ignition (HCCI) reaches peak efficiencies of 48%, the direct injection (DI) develops the best power output on the shaft with higher efficiencies throughout the load range. Figure 25 shows that direct injection stands out due to lower cooling losses since combustion takes place closest to the piston top dead centre (TDC).

LOSSES	Diesel DI (Diesel oil)	HCCI (H_2)	DIH_2 (H_2)
Shaft [%]	27.9	48.0	42.8
Cooling [%]	42.2	20.4	17.3
Exhaust [%]	35.3	31.6	39.9
Shaft Power [W]	9000	7076	10280

Figure 25: Losses in hydrogen engine (Antunes, 2010).

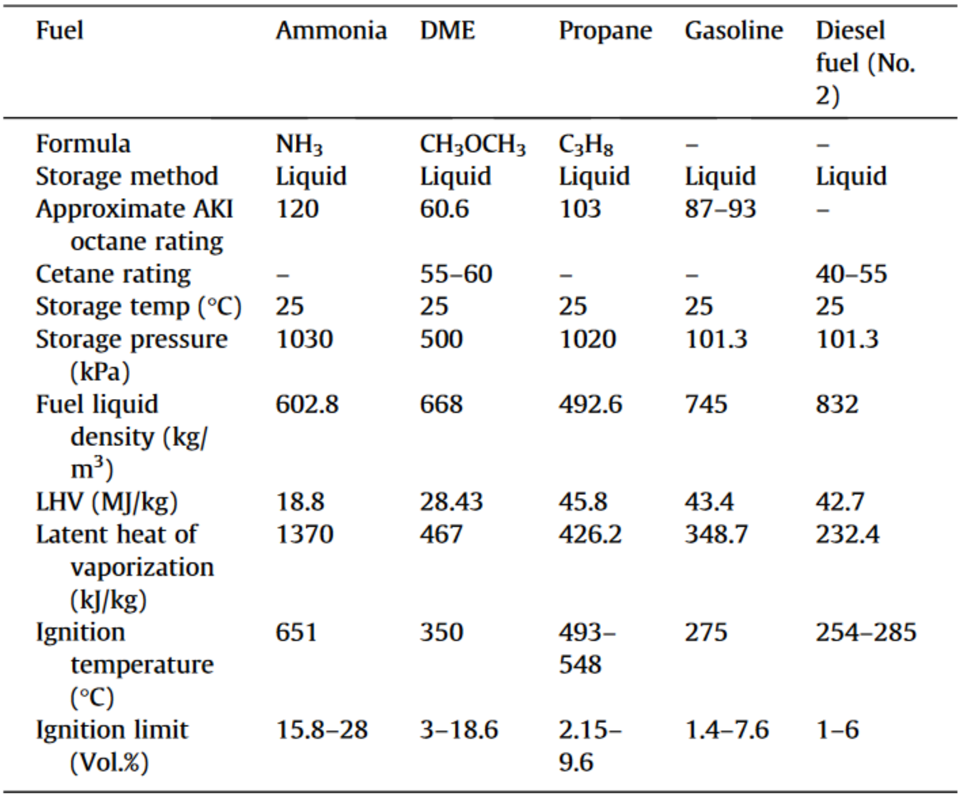
It must be concluded that it can be advantageous to operate an internal combustion engine on hydrogen, especially with direct injection technology. However, due to pre-ignition problems and a high autoignition temperature, the engine operation and control is sophisticated. Although carbon emissions can be avoided, the formation of nitrogen oxides occurs due to the high compression ratios and combustion temperatures. Reductions of NOx by 20% compared to the engine running on diesel can be examined though (Antunes, 2010).

3.3.2. Ammonia

Ammonia as a fuel is not an entirely new idea. During the Second World War, Belgium introduced a fleet of 100 buses running on ammonia, due to the shortage of diesel fuel (Kroch, 1945). Back then, a blend of ammonia with coal gas as a combustion promoter was used. The gasification of coal, as well as the Haber-Bosch process for the ammonia synthesis, were already known that time and the independence of imports was a matter of survival. The buses have been in use for months without major issues (*ibid*). In regions were ammonia is a commonly used substance for agriculture such as the middle-west of the United States, liquid ammonia can be easily implemented as a fuel for internal combustion engines of agricultural machinery.

As described in Chapter 2.2.2, ammonia has some interesting properties such as its high hydrogen content and the absence of carbon atoms. It is also an attractive fuel due to its high-octane rate of approximately 110, allowing high compression and a good thermodynamic efficiency (Zamfirescu and Dincer, 2009). Narrow flammability limits imply good safety and low explosion danger when properly transported (*ibid*).

Table 3 shows the fuel properties of ammonia compared to other conventional and non-conventional fuels.



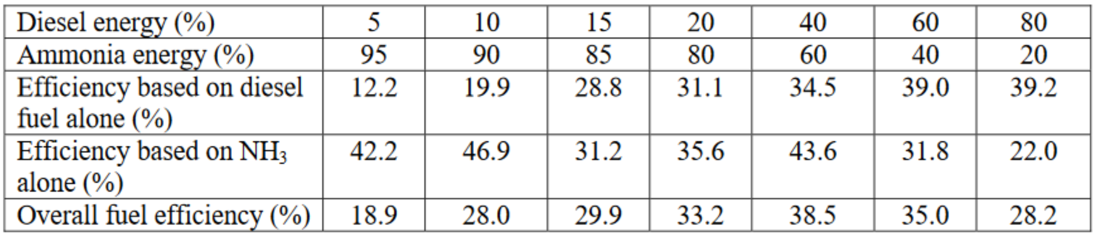
Fuel	Ammonia	DME	Propane	Gasoline	Diesel fuel (No. 2)
Formula	NH_3	CH_3OCH_3	C_3H_8	–	–
Storage method	Liquid	Liquid	Liquid	Liquid	Liquid
Approximate AKI octane rating	120	60.6	103	87–93	–
Cetane rating	–	55–60	–	–	40–55
Storage temp (°C)	25	25	25	25	25
Storage pressure (kPa)	1030	500	1020	101.3	101.3
Fuel liquid density (kg/m^3)	602.8	668	492.6	745	832
LHV (MJ/kg)	18.8	28.43	45.8	43.4	42.7
Latent heat of vaporization (kJ/kg)	1370	467	426.2	348.7	232.4
Ignition temperature (°C)	651	350	493–548	275	254–285
Ignition limit (Vol.%)	15.8–28	3–18.6	2.15–9.6	1.4–7.6	1–6

Table 3: Comparison of combustion properties of different fuels (Ryu, et al., 2014).

Just like the previously discussed hydrogen properties, ammonia has a very high auto-ignition temperature of 651°C and a high heat of vaporisation of 1370 kJ per kilogram. The high ignition temperature delays the time of ignition and the high latent heat of vaporization reduces the combustion temperature due to fast vaporization. Consequently, the operation is within a very restricted range. Ammonia can only be combusted between 16-28% of volume in air and together with its low flame speed a combustion promoter is required to run ammonia in a conventional combustion engine (Zamfirescu and Dincer, 2009). Compression-ignition engines just using ammonia as a fuel require compression ratios of 35:1 to reach the high auto-ignition temperature (Reiter, 2009). Ignition delay increases with higher rotational speed than 900 rpm (*ibid*). After all, experimental results show that ammonia as a mono-fuel in compression ignition engines is not feasible and combustion promoters are necessary. In spark-ignition engines the main problem appears to be the low efficiency, the need for strong spark plugs to overcome the resistance to ignition and the need of partly dissociation of ammonia prior to the intake with a weight concentration of at least 5% hydrogen (Starkman and Smith, 1966).

Another study carried out by researchers at the University of Pisa in Italy, describes the optimum hydrogen content with 7% to power a 505 cm³ twin-cylinder spark-ignition engine (Frigo, et al., 2012).

Table 4 gives an overview of fuel efficiencies of different operating conditions based on a diesel-ammonia dual-fuel engine (Kong, 2008). The investigation shows that the best overall efficiency occurs at a fuel-mixture between 40-60% ammonia content, reaching values of 35-38.5% (*ibid*). However, using a fuel composition of 95% ammonia and 5% diesel results in an overall fuel efficiency of only 18.9% (*ibid*). Calculations are based on the engine power output over the fuel energy input. Engine specification can be found in appendix A. Furthermore, due to a limited combustion efficiency of ammonia, exhaust ammonia emissions of 5% have been noticed.



Diesel energy (%)	5	10	15	20	40	60	80
Ammonia energy (%)	95	90	85	80	60	40	20
Efficiency based on diesel fuel alone (%)	12.2	19.9	28.8	31.1	34.5	39.0	39.2
Efficiency based on NH_3 alone (%)	42.2	46.9	31.2	35.6	43.6	31.8	22.0
Overall fuel efficiency (%)	18.9	28.0	29.9	33.2	38.5	35.0	28.2

Table 4: Efficiencies of ammonia-diesel fuel engine (Kong, 2008).

After all, it can be said that ammonia-based engines are far away from being commercially available with only a few test results accessible. Ammonia always requires combustion promoters inevitably causing emissions, especially nitrogen oxide. It is very unlikely that this concept will establish on a large scale in the shipping industry.

3.3.3. Methanol

Methanol is one of the most common non-conventional fuels in the transport sector with good experience both on road and at the sea. Countries like China, who do not have much oil production but extensive coal resources, have been producing methanol from coal for decades (Andersson and Salazar, 2015). Even though the environmental impact is bad for using coal as a feedstock, the infrastructure can be used for future production based on a biomass feedstock. After the oil crisis in the 1970s, the United States performed a large-scale test for the conversion of gasoline vehicles to 85%

methanol, still known as M85 fuel (*ibid*). Technically, the programme was successful with energy efficiency levels comparable to conventional gasoline vehicles, but cheaper oil prices stopped the expansion.

Ship engines require high efficiency, high torque and a low rotational speed, and thus usually compression ignition engines running on HFO or diesel are used. Methanol is very universal and can be used in both petrol and diesel engines. Its high knock resistance and high heat of vaporization allow high compression ratios which enable higher thermal efficiency than petrol (Zhen, 2017). The availability of methanol, the convenience of using existing infrastructure with conventional storage tanks as well as the simplicity of engine design made it the first-choice fuel for the retrofitting of the multi-megawatt vessel Stena Germanica (Andersson and Salazar, 2015). Using methanol in diesel engines is possible, but its lower cetane number needs ignition improvers to avoid ignition delay. This can be done by diesel as an additive to methanol or by additional glow plugs. For the Stena Germanica, a two-stroke eight-cylinder 6 MW engine from Wartsila has been modified to run on methanol with adaptions such as high-pressure methanol pumps, modified cylinder heads, a common rail system for methanol injection and a double-walled piping (Haraldson and Wärtsilä, 2015).

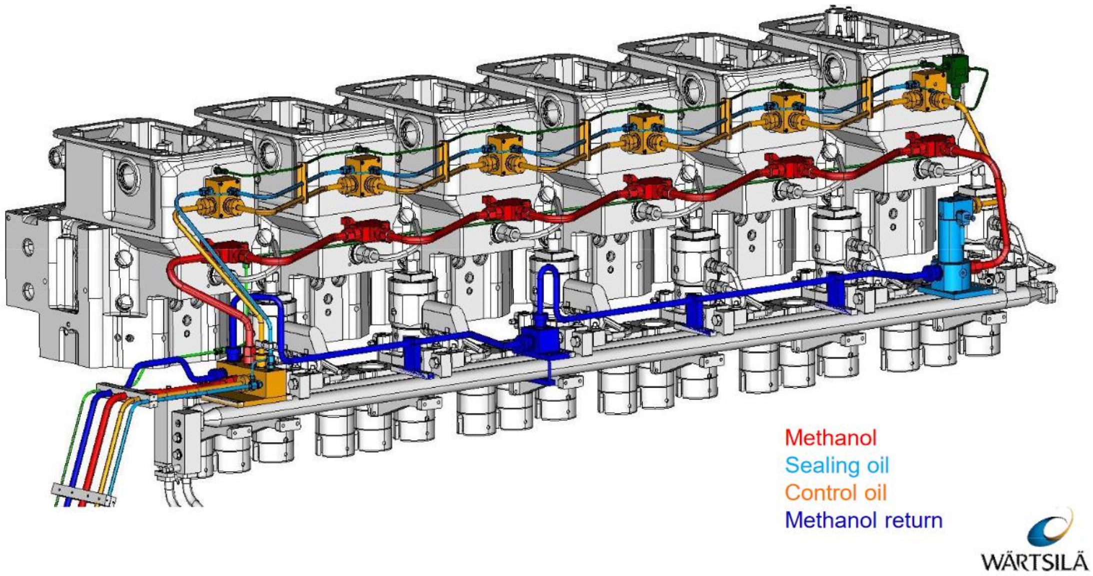
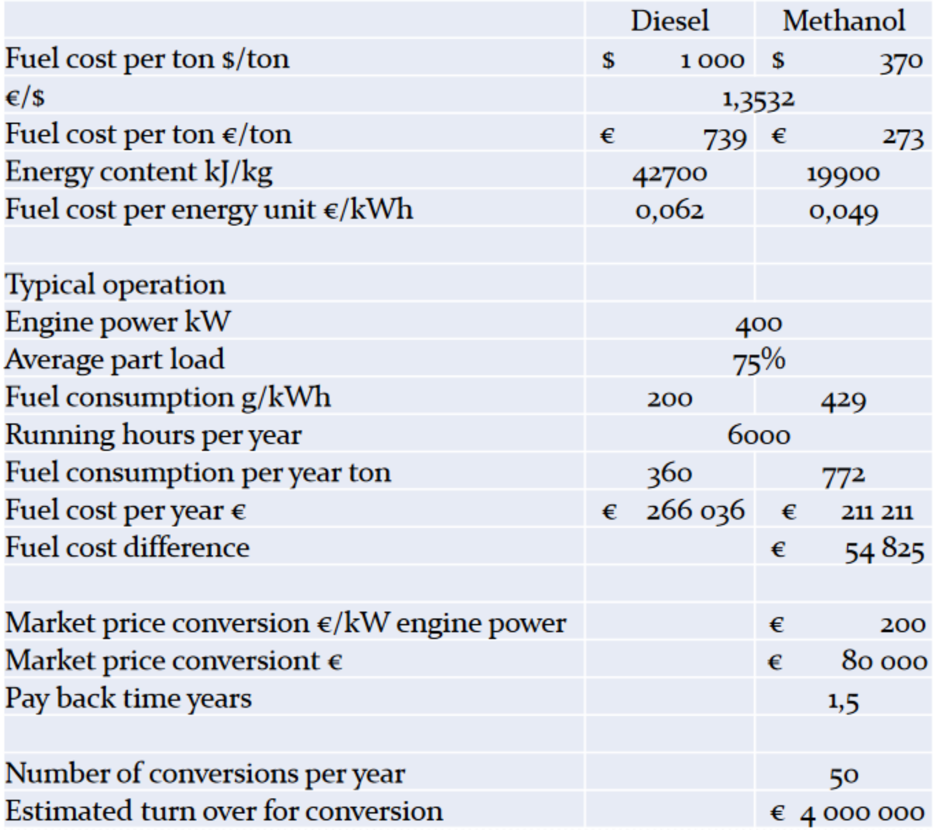


Figure 26: Converted diesel engine running on methanol (Haraldson and Wärtsilä, 2015).

The ferry is in operation since March 2015, recording a slightly lower fuel consumption, a reduction of sulphur oxide by 99%, particles by 95%, nitrogen oxide by 60% and CO2 by 25%, compared to the previous engine (Stena Line, 2015). Furthermore, the company claims that the efficiency and power output is equal compared to the operation on diesel with 40.9% at 75% load (Haraldson and Wärtsilä, 2015).

Table 5 compares the technical and economical values of diesel and methanol engines with the same power output and the same running hours per year. Since a detailed economical view is not within the scope of this report, special attention should be paid to the difference in fuel consumption. The table clearly shows that the fuel consumption of methanol is significantly higher than the diesel consumption, due to a lower energy density of methanol. Considering the difference in volumetric density, it also requires larger tanks to store the methanol. However, considering 45 MJ/kg for diesel and 22.65 MJ/kg for methanol, the efficiencies based on the power output over the fuel input is quite comparable, having 53.3% for diesel and 49.4% for methanol.



	Diesel	Methanol
Fuel cost per ton $/ton	$ 1 000	$ 370
€/$	1,3532	
Fuel cost per ton €/ton	€ 739	€ 273
Energy content kJ/kg	42700	19900
Fuel cost per energy unit €/kWh	0,062	0,049
Typical operation		
Engine power kW	400	
Average part load	75%	
Fuel consumption g/kWh	200	429
Running hours per year	6000	
Fuel consumption per year ton	360	772
Fuel cost per year €	€ 266 036	€ 211 211
Fuel cost difference		€ 54 825
Market price conversion €/kW engine power		€ 200
Market price conversiont €		€ 80 000
Pay back time years		1,5
Number of conversions per year		50
Estimated turn over for conversion		€ 4 000 000

Table 5: Comparison of diesel and methanol engines with the same power (Fagerlund, 2014).

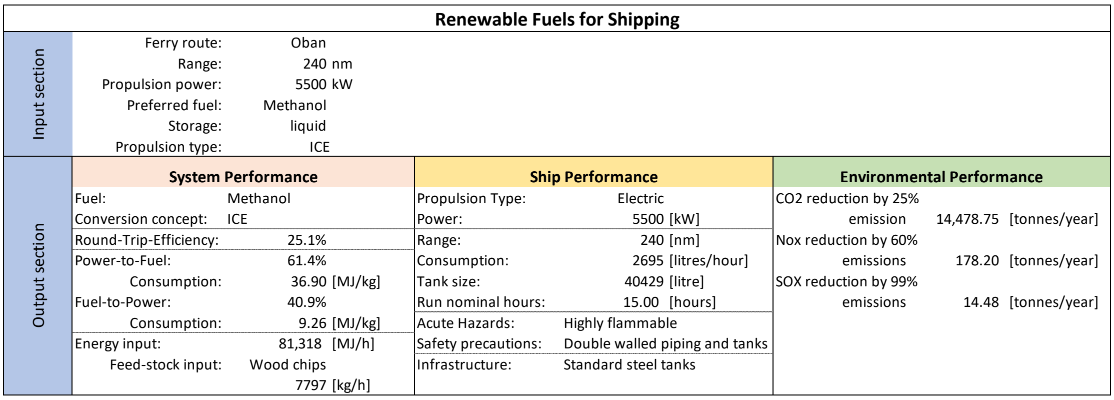
Methanol is the most developed alternative fuel for shipping requiring only minor changes to the existing infrastructure and conventional engine design. If the production is based on biomass feedstock the approach of using methanol as a shipping fuel might be the easiest to achieve significant emission reductions.

4. Analysis Tool for Marine Fuels

4.1. Tool Description

The tool “Renewable Fuels for Shipping”, is supposed to enable the user a rough estimation of system efficiency, fuel consumption, tank size, safety, infrastructure and emissions as a result of some basic input parameters such as range, propulsion power and preferred fuel.

The tool is based on specifications from the CALMAC ferry “MV Clansman” with a gross tonnage of 5,500 and an overall length of 100 metres. The propulsion power is 5.5 MW and the range must be at least 240 nautical miles a day in order to operate safely on the main route between Oban and Castlebay on the Isle of Barra. A safety margin of 25% additional range to the standard route is included. Further specifications about the “MV Clansman” and the route can be found in Appendix B. The tool is built to be suitable for other ships and other routes as well. Adjustments can be done by changing the parameters in the input section.



Renewable Fuels for Shipping

Input section	Ferry route:	Oban	
	Range:	240	nm
	Propulsion power:	5500	kW
	Preferred fuel:	Methanol	
	Storage:	liquid	
	Propulsion type:	ICE	

	System Performance			Ship Performance			Environmental Performance		
Output section	Fuel:	Methanol		Propulsion Type:	Electric		CO2 reduction by 25%		
	Conversion concept:	ICE		Power:	5500	[kW]	emission	14,478.75	[tonnes/year]
	Round-Trip-Efficiency:	25.1%		Range:	240	[nm]	Nox reduction by 60%		
	Power-to-Fuel:	61.4%		Consumption:	2695	[litres/hour]	emissions	178.20	[tonnes/year]
	Consumption:	36.90	[MJ/kg]	Tank size:	40429	[litre]	SOX reduction by 99%		
	Fuel-to-Power:	40.9%		Run nominal hours:	15.00	[hours]	emissions	14.48	[tonnes/year]
	Consumption:	9.26	[MJ/kg]	Acute Hazards:	Highly flammable				
	Energy input:	81,318	[MJ/h]	Safety precautions:	Double walled piping and tanks				
	Feed-stock input:	Wood chips		Infrastructure:	Standard steel tanks				
		7797	[kg/h]						

Table 6: Example of the tool overview based on methanol combustion engine (Source: Own design).

Basically, the tool can be used for any fuel regardless of how the fuel is produced and which resources used. Nevertheless, the aim of this tool is considering fuels based on the carbon-free closed hydrogen cycle but also fuels based on the closed carbon cycle, using a sustainable feedstock for the fuel production.

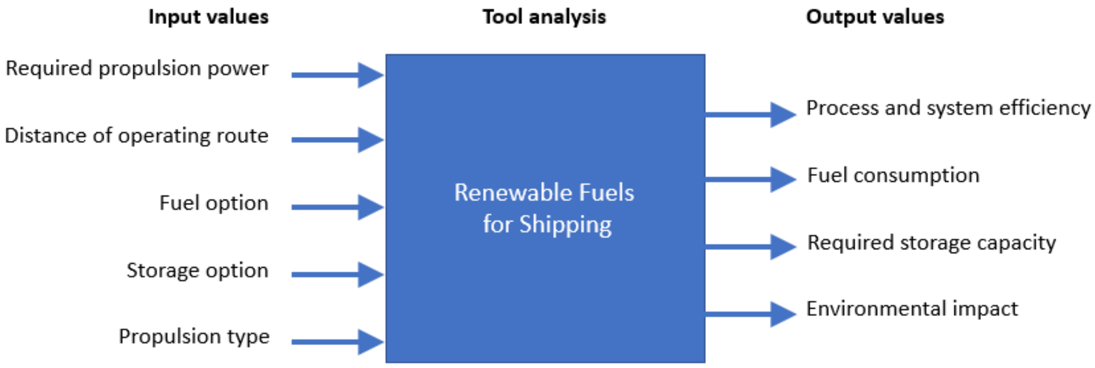


Figure 27: Input and output parameters for tool analysis (Source: Own design).

The main input parameters as listed on the left-hand side in Figure 27, are required to calculate the appropriate output values. The fuel properties are based on literature research and provide the necessary figures for the calculations. The numbers for specific energy consumption and efficiency of conversion processes are also based on literature which is indicated by footnotes on the bottom of each of the following tables.

The output parameters are split into three sections, as shown in the tool overview sheet in Table 6. The first section is about system performance, describing the main conversion processes from feedstock input to fuel output and from fuel to power output. Overall system efficiency, as well as process efficiency, are part of the results. The section ship performance considers fuel consumption and required tank size for the predefined range. The number of hours the ship can run on full load is in place of the distance the ship can travel before the tank is empty. A minimum of 15h operation on full load (16 knots) is set as a requirement to sail the route from Oban to Castlebay and return safely. Moreover, in this section, the actual hazards of the chosen fuel and its precautions, as well as infrastructure requirements, are mentioned. Eventually, the environmental performance lists the reduction of emissions compared to the previously combusted marine fuel oil.

The following sections describe all the necessary calculations of the tool analysis. Three proposed fuels are investigated in detail, to find the best suitable renewable fuel for the specific vessel.

4.2. Analysis of Ammonia

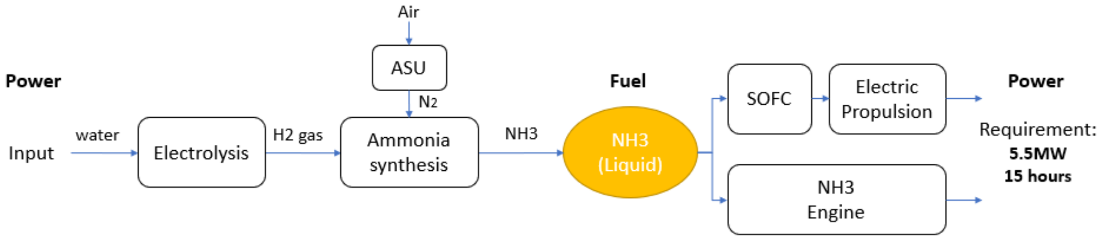
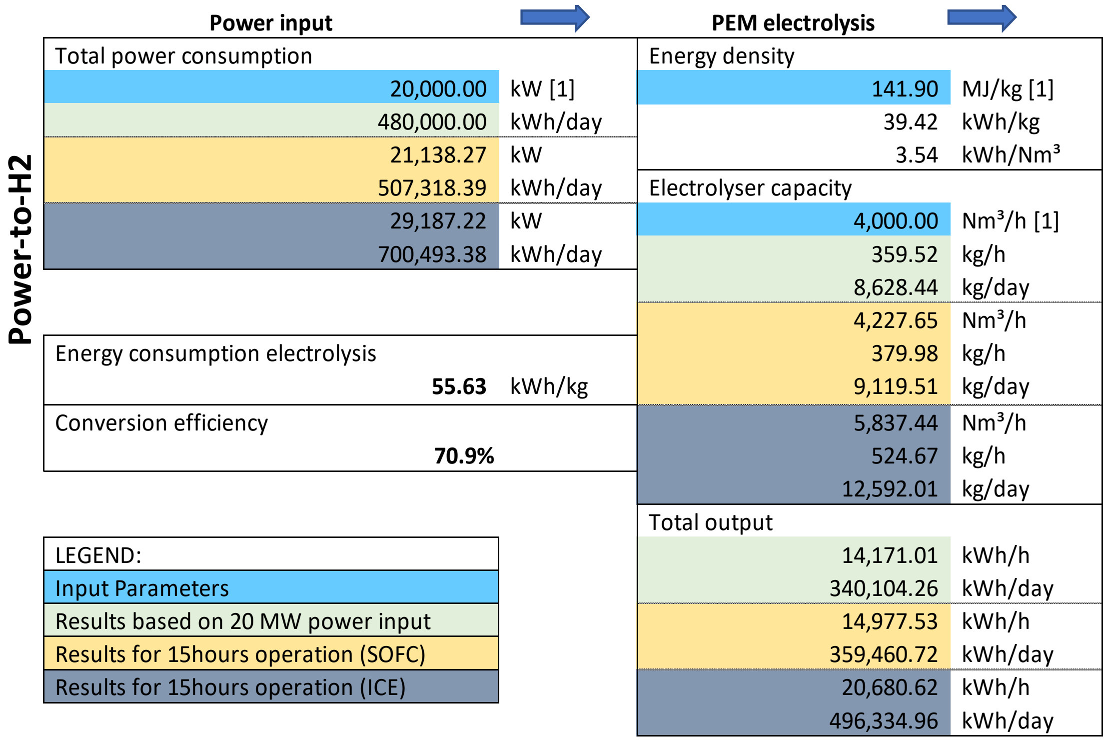


Figure 28: Block diagram of ammonia processes (Source: Own design).

The conversion processes for the system power-to-ammonia-to-power is mainly based on a feasibility study by Morgan (2013) and manufacturers product sheets. As described in Chapter 2.2.2, the first conversion step is the electrolysis of water into hydrogen gas. The electrolyser used is a purchasable proton-exchange membrane (PEM) module from the Canadian company Hydrogenics. Each of the “Hylyzer-400-30” modules have 2 MW input power and 400 Nm³/h[1] hydrogen production.



Power input

Total power consumption	
20,000.00	kW [1]
480,000.00	kWh/day
21,138.27	kW
507,318.39	kWh/day
29,187.22	kW
700,493.38	kWh/day
Energy consumption electrolysis	
55.63	kWh/kg
Conversion efficiency	
70.9%	

PEM electrolysis

Energy density	
141.90	MJ/kg [1]
39.42	kWh/kg
3.54	kWh/Nm³
Electrolyser capacity	
4,000.00	Nm³/h [1]
359.52	kg/h
8,628.44	kg/day
4,227.65	Nm³/h
379.98	kg/h
9,119.51	kg/day
5,837.44	Nm³/h
524.67	kg/h
12,592.01	kg/day
Total output	
14,171.01	kWh/h
340,104.26	kWh/day
14,977.53	kWh/h
359,460.72	kWh/day
20,680.62	kWh/h
496,334.96	kWh/day

LEGEND:
Input Parameters
Results based on 20 MW power input
Results for 15hours operation (SOFC)
Results for 15hours operation (ICE)

Table 7: Ammonia: Power-to-hydrogen [1] (Hydrogenics, 2016).

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[1] 1 kg = 11.126 Nm³ (Hydrogenics, 2016).

Depending on the input parameters, the number of modules needed can be obtained by the results. Further details about the module can be found in Appendix C. The conversion from power to hydrogen is the most energy intensive process for the production of ammonia with around 29% of the energy lost.

In the first place, some input parameters need to be assumed to create the tool. Therefore, ten of the modules were assumed with a total input of 20 MW to calculate the conversion efficiency and the specific energy consumption, which can be used for the reverse calculation later. A conversion efficiency of 70.9% can be achieved with these modules, gaining 4000 norm cubic metres per hour of 99.998% hydrogen gas at 30 bar (Hydrogenics, 2016). Under the presumption of 20 MW input, the energy content of produced hydrogen is 14.17 MW or 340 MWh per day. In order to determine the required input power to meet the demand of the 5.5 MW ship propulsion for 15 hours, a reverse calculation based on the following steps is conducted. As described in the legend in Table 7, the numbers highlighted in yellow represent the values if a fuel cell in combination with an electrical engine is used as propulsion type. The values highlighted in grey represent values for powering an internal combustion engine. Comparing the results, it already appears that the fuel cell requires less energy input to meet the propulsion requirements. However, this will be discussed more detailed in Chapter 5.

The hydrogen gas is fed into the ammonia synthesis reactor to form ammonia with nitrogen from the air separation unit (ASU). The energy required for the synthesis itself is slightly over 7 kWh per kg of ammonia produced and is primarily consumed by compression of the hydrogen and nitrogen gases to reach 150 bar for the process conditions. Together with the energy required for the ASU and the MVC, almost 88% of the energy contained in the hydrogen can be obtained as ammonia. The combined efficiency of the electrolysis and the ammonia synthesis is 62.3%, which is quite comparable to the value of Morgan (2013), stating the overall conversion from power to NH3 of 66.4% efficiency. The difference might derive from the different electrolyser used in the analysis, which is the more state of the art module than the one described by Morgan (2013).

H2-to-NH3

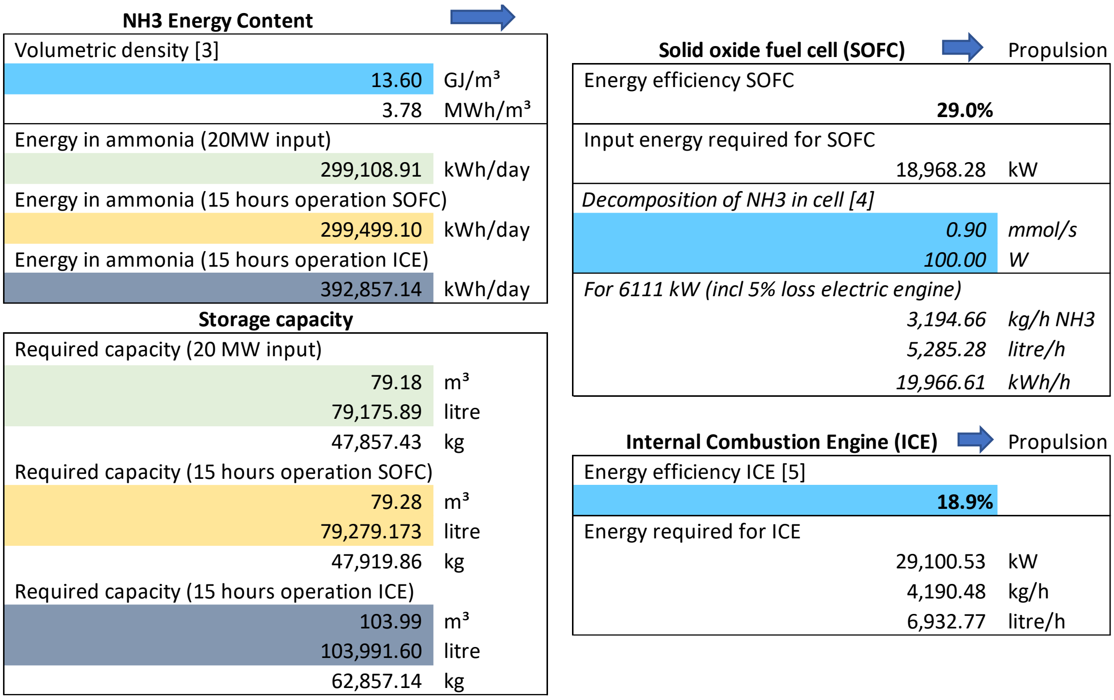
H2 energy			Ru-based Synthesis		
Output electrolysis			Energy density ammonia		
	340,104.26	kWh/day		22.50	MJ/kg [3]
	359,460.72	kWh/day		6.25	kWh/kg
	496,334.96	kWh/day	Energy consumption synthesis		
Energy losses in ammonia synthesis [2]				**7.11**	kWh/kg
ASU			Conversion efficiency		
	0.09	*kWh/kgNH3*		**87.9%**	
MVC			Output		
	0.02	*kWh/kgNH3*		47,857.43	kg/day
Synthesis loop				299,108.91	kWh/day
	0.64	*kWh/kgNH3*		50,581.15	kg/day
	0.75	*kWh/kgNH3*		316,132.19	kWh/day
Feedstock requirement [2]				69,841.27	kg/day
Nitrogen				436,507.94	kWh/day
	0.82	*kg/kgNH3*	Conversion losses		
Hydrogen				0.75	kWh/kg [2]
	0.18	*kg/kgNH3*		40,995.35	kWh/day
Water				43,328.53	kWh/day
	1.67	*kg/kgNH3*		59,827.03	kWh/day

Table 8: Ammonia: hydrogen to ammonia [2] (Morgan, 2013); [3] (Wang, et al., 2013).

On the left-hand side in Table 8, the losses through the different processes required for the ammonia synthesis are listed. Furthermore, the feedstock requirements are estimated only consisting of nitrogen and hydrogen for the synthesis and water for the electrolysis.

The output of ammonia in mass and in energy units is a result of the input from the electrolysis minus the conversion losses. This process step is the last of the onshore fuel production site. The fuel is ready for distribution and storage. Ammonia is usually stored in liquid form under a pressure of 10 bar in double-walled steel tanks. Due to the volumetric heating value of liquid ammonia of 13.6 GJ/m³ (Wang, et al., 2013), the size of the tank must be about 80m³ to meet the demand of the shaft power for 15 hours (see Table 9).

There are two different concepts for the ship propulsion. The first being the application of an ammonia fed SOFC in combination with an electrical engine. As described in Chapter 3.2.2, the SOFC converts ammonia directly into electrical power by decomposing the molecules at the fuel cells anode into hydrogen and nitrogen. The conversion efficiency of the fuel cell is based on the reaction flow rate carried out by Alagharu (2010). Calculations in Table 9 result in 29% conversion efficiency which also fits other literature and appears to be a reasonable value. To ensure a shaft power of 5.5 MW, the power provided for the electrical propulsion must be 5.79 MW including a 5% loss in the electrical engine. The fuel cell consumes close to 5,300 litres of ammonia per hour to provide this amount of energy. The daily produced amount of ammonia must be 285 MWh to run the system for 15 hours.



NH3 Energy Content →		
Volumetric density [3]		
	13.60	GJ/m^3
	3.78	MWh/m^3
Energy in ammonia (20MW input)		
	299,108.91	kWh/day
Energy in ammonia (15 hours operation SOFC)		
	299,499.10	kWh/day
Energy in ammonia (15 hours operation ICE)		
	392,857.14	kWh/day
Storage capacity		
Required capacity (20 MW input)		
	79.18	m^3
	79,175.89	litre
	47,857.43	kg
Required capacity (15 hours operation SOFC)		
	79.28	m^3
	79,279.173	litre
	47,919.86	kg
Required capacity (15 hours operation ICE)		
	103.99	m^3
	103,991.60	litre
	62,857.14	kg

Solid oxide fuel cell (SOFC) →		Propulsion
Energy efficiency SOFC		
	29.0%	
Input energy required for SOFC		
	18,968.28	kW
Decomposition of NH3 in cell [4]		
	0.90	*mmol/s*
	100.00	*W*
For 6111 kW (incl 5% loss electric engine)		
	3,194.66	*kg/h NH3*
	5,285.28	*litre/h*
	19,966.61	*kWh/h*

Internal Combustion Engine (ICE) →		Propulsion
Energy efficiency ICE [5]		
	18.9%	
Energy required for ICE		
	29,100.53	kW
	4,190.48	kg/h
	6,932.77	litre/h

Table 9: Ammonia: Fuel-to-power [3] (Wang, et al., 2013); [4] (Alagharu, et al., 2010); [5] (Kong, 2008).

The second approach is the application of an internal combustion engine running on 90% ammonia and 10% hydrogen. The engine as described in Chapter 2.2.2. has an efficiency of 19% (Kong, 2008). Including a 10% hydrogen mixture in the fuel, the ammonia consumption is still about 7,000 litres per hour and clearly performs poorer than the SOFC.

Propulsion power

	5,500.00	kW
Power for electric engine with 5% losses		
	5,789.47	kW
NH3 Solid Oxide Fuel Cell		
15 hours basic requirement		
	15.00	h
Duration on full load (15 kW input)		
	14.98	h
Round-trip-efficiency		
	17.2%	
NH3 Internal Combustion Engine		
15 hours basic requirement		
	15.00	h
Duration on full load (15 kW input)		
	11.42	h
Round-trip-efficiency		
	11.8%	

Table 10: Output of ammonia concepts (Source: Own design).

Even though the SOFC needs an additional component to power the ship, the overall efficiency is significantly better compared to the internal combustion engine. The overall efficiency of the ammonia concept with SOFC and electric propulsion is 17.2%, whereas the system efficiency of the concept with an internal combustion engine is only 11.8%. However, the calculations are based on numbers from literature models which have been created under certain circumstances and might not be a hundred per cent appropriate for this study.

4.3. Analysis of Hydrogen

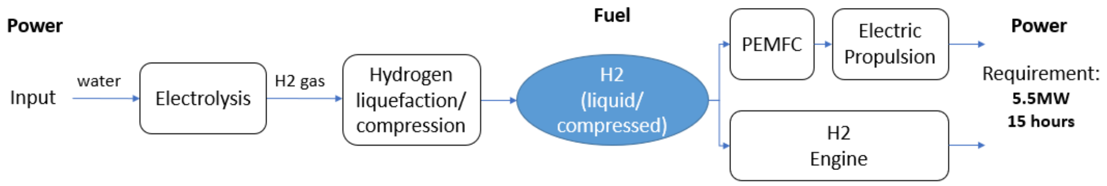
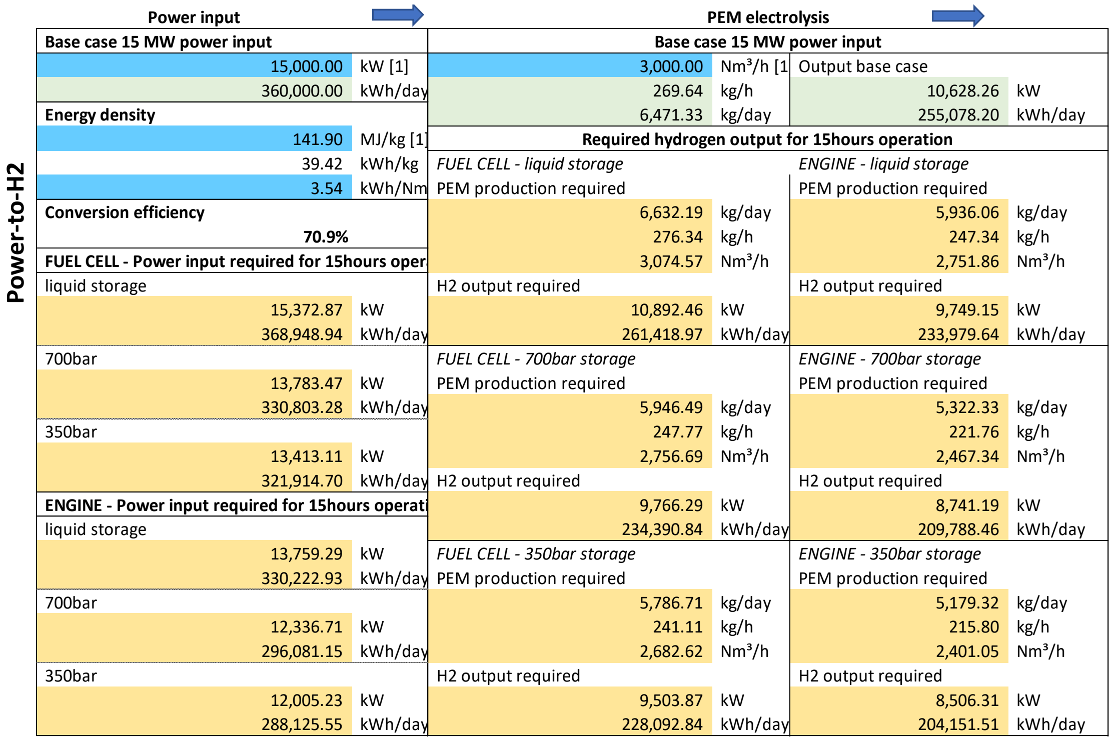


Figure 29: Block diagram of hydrogen processes (Source: Own design).

Although it is known that the storage of pure hydrogen is associated with some issues, it makes sense to have a closer look at hydrogen as a storage medium. The only feedstock needed is water, which can be converted into hydrogen by electrolysis. The chosen approach considers the assumption of specific conversion parameters to get some outputs in the first place. In order to meet the output requirements for the ferry service, the appropriate input parameters need to be adjusted by recalculation. There are three different storage options and two different propulsion concepts considered, resulting in six different solutions and one base case. The base case assumes one “Hylyzer 3000-30” module with 15 MW input power and 3,000 Nm³/h (norm cubic metres per hour) of hydrogen production (see Appendix C). The calculated efficiency is 71% and the hydrogen production amounts to 255 MWh.

Having a broader look at the concepts in Table 11, the range for the input energy is between 12-15.4 MW for the same number of hours operation and the same shaft power. The required hydrogen production ranges from 204-261 MWh for an equal output. This is on the one hand due to different losses through work requirements of storage concepts as described in Table 12 and on the other hand because of different losses in the fuel cells compared to the internal combustion engine as described in Table 13.

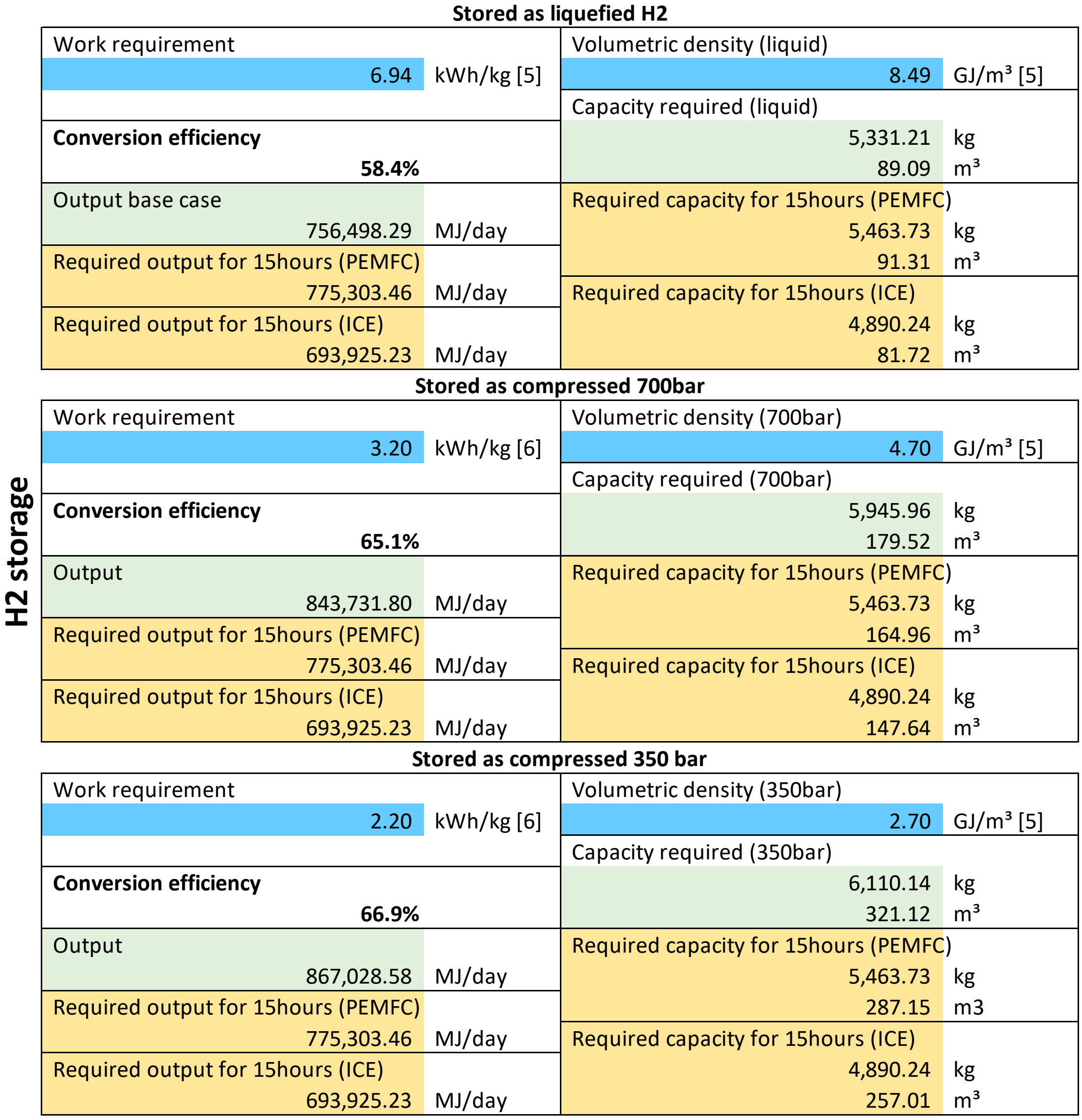


Power-to-H2

Power input			**PEM electrolysis**					
Base case 15 MW power input			**Base case 15 MW power input**					
	15,000.00	kW [1]		3,000.00	Nm³/h [1	Output base case		
	360,000.00	kWh/day		269.64	kg/h		10,628.26	kW
Energy density				6,471.33	kg/day		255,078.20	kWh/day
	141.90	MJ/kg [1]	**Required hydrogen output for 15hours operation**					
	39.42	kWh/kg	*FUEL CELL - liquid storage*			*ENGINE - liquid storage*		
	3.54	kWh/Nm	PEM production required			PEM production required		
Conversion efficiency				6,632.19	kg/day		5,936.06	kg/day
	70.9%			276.34	kg/h		247.34	kg/h
FUEL CELL - Power input required for 15hours oper				3,074.57	Nm³/h		2,751.86	Nm³/h
liquid storage			H2 output required			H2 output required		
	15,372.87	kW		10,892.46	kW		9,749.15	kW
	368,948.94	kWh/day		261,418.97	kWh/day		233,979.64	kWh/day
700bar			*FUEL CELL - 700bar storage*			*ENGINE - 700bar storage*		
	13,783.47	kW	PEM production required			PEM production required		
	330,803.28	kWh/day		5,946.49	kg/day		5,322.33	kg/day
350bar				247.77	kg/h		221.76	kg/h
	13,413.11	kW		2,756.69	Nm³/h		2,467.34	Nm³/h
	321,914.70	kWh/day	H2 output required			H2 output required		
ENGINE - Power input required for 15hours operati				9,766.29	kW		8,741.19	kW
liquid storage				234,390.84	kWh/day		209,788.46	kWh/day
	13,759.29	kW	*FUEL CELL - 350bar storage*			*ENGINE - 350bar storage*		
	330,222.93	kWh/day	PEM production required			PEM production required		
700bar				5,786.71	kg/day		5,179.32	kg/day
	12,336.71	kW		241.11	kg/h		215.80	kg/h
	296,081.15	kWh/day		2,682.62	Nm³/h		2,401.05	Nm³/h
350bar			H2 output required			H2 output required		
	12,005.23	kW		9,503.87	kW		8,506.31	kW
	288,125.55	kWh/day		228,092.84	kWh/day		204,151.51	kWh/day

Table 11: Hydrogen: Power-to-fuel [1] (Hydrogenics, 2016).

As soon as hydrogen gas is produced by the electrolysis, it needs to be distributed and stored. Table 12 shows the work requirements for compression and liquefication of hydrogen gas provided from the electrolyser at 30 bar. The values based on Gardiner (2009) and Valenti (2016), have 20 bar and 300 K as starting conditions though. However, due to the small specific difference from 20 bar to 30 bar, it is neglected.



H2 storage

Stored as liquefied H2

Work requirement	6.94	kWh/kg [5]	Volumetric density (liquid)	8.49	GJ/m^3 [5]
Conversion efficiency	**58.4%**		Capacity required (liquid)	5,331.21 89.09	kg m^3
Output base case	756,498.29	MJ/day	Required capacity for 15hours (PEMFC)	5,463.73 91.31	kg m^3
Required output for 15hours (PEMFC)	775,303.46	MJ/day			
Required output for 15hours (ICE)	693,925.23	MJ/day	Required capacity for 15hours (ICE)	4,890.24 81.72	kg m^3

Stored as compressed 700bar

Work requirement	3.20	kWh/kg [6]	Volumetric density (700bar)	4.70	GJ/m^3 [5]
Conversion efficiency	**65.1%**		Capacity required (700bar)	5,945.96 179.52	kg m^3
Output	843,731.80	MJ/day	Required capacity for 15hours (PEMFC)	5,463.73 164.96	kg m^3
Required output for 15hours (PEMFC)	775,303.46	MJ/day			
Required output for 15hours (ICE)	693,925.23	MJ/day	Required capacity for 15hours (ICE)	4,890.24 147.64	kg m^3

Stored as compressed 350 bar

Work requirement	2.20	kWh/kg [6]	Volumetric density (350bar)	2.70	GJ/m^3 [5]
Conversion efficiency	**66.9%**		Capacity required (350bar)	6,110.14 321.12	kg m^3
Output	867,028.58	MJ/day	Required capacity for 15hours (PEMFC)	5,463.73 287.15	kg m3
Required output for 15hours (PEMFC)	775,303.46	MJ/day			
Required output for 15hours (ICE)	693,925.23	MJ/day	Required capacity for 15hours (ICE)	4,890.24 257.01	kg m^3

Table 12: Hydrogen storage options [5] (Valenti, 2016); [6] (Gardiner, 2009).

The liquefication consumes most energy with almost 7 kWh per kg of hydrogen. Thus, the conversion efficiency from water to liquefied hydrogen decreases to 58%. The storage capacity required is quite low due to the high energy density of hydrogen in liquid form. However, more than 91m^3 are needed which is almost 11m^3 more compared to the ammonia concept meeting the same output requirements. If hydrogen gets compressed the results are even worse, demanding almost double the volume for the same amount of energy at 700 bar. Mentionable is the clearly lower work input of 3.2 kWh/kg pushing the efficiency up to 65%. The most common storage pressure for non-stationary hydrogen is 350 bar, which can be found in some hydrogen vehicles already. The work requirement for the compression to 350 bar is only 2.2 kWh/kg hydrogen but the storage capacity for 215 MWh produced hydrogen requires about 287m^3 in volume. This is a spherical pressure tank with almost 8.5m in diameter.

H2-to-Power

PEM fuel cell ➡		Propulsion	**Internal Combustion Engine (ICE)** ➡		Propulsion
Energy consumption FC (per MW)			Energy consumption ICE		
	700.00	Nm^3/h [8]		3,627.25	Nm^3/h
	11.13	Nm^3/kg		326.02	kg H2/h
	3.54	kWh/Nm3			
	2,479.93	kW			
	62.92	kg H2			
Efficiency PEMFC			**Engine thermal efficiency**		
	40.3%			**42.8%**	[4]
Energy required for propulsion power			Energy required for propulsion		
	4,052.63	Nm^3/h		326.02	kg H2/h
	364.25	kg H2/h		12,850.47	kW
	14,357.47	kW			
Propulsion power (required)			Propulsion power (required)		
	5,500.00	kW		5,500.00	kW
Power for electric engine with 5% losses					
	5,789.47	kW			
Duration on full load:			Duration on full load:		
15 hours basic requirement			15 hours basic requirement		
	15.00	h		15.00	h
liquid			liquid		
	14.64	h		16.35	h
700bar			700bar		
	16.32	h		18.24	h
350bar			350bar		
	16.77	h		18.74	h
Round-trip-efficiencies:			**Round-trip-efficiencies:**		
liquid			liquid		
	22.4%			**25.0%**	
700bar			700bar		
	24.9%			**27.9%**	
350bar			350bar		
	25.6%			**28.6%**	

Table 13: Hydrogen: Fuel-to- power [4] (Antunes, 2010); [8] (Ballard, 2012).

The further conversion from hydrogen back to power can be done by fuel cells or internal combustion engines. Latter is not very common, but test results of engines running on hydrogen have been promising and need to be considered too. As already described in Chapter 3.3.1, studies from Antunes (2010) show that thermal efficiencies of almost 43% can be achieved if a direct injection of hydrogen is applied. Even if this is just a theoretical number and hardly achievable under real circumstances, it must not be disregarded. The conversion efficiency of the PEM fuel cell is probably a more realistic number because it is based on a purchasable unit from one of the leading fuel cell manufacturers Ballard Power Systems Inc., indicating an efficiency of 40.3% from hydrogen to power (Balllard, 2012).

Assuming an input power of 15 MW around the clock, the shaft power of 5.5 MW can only be delivered for a bit over 14 hours, if liquefaction of hydrogen is considered. The round-trip-efficiency is 22.4% including losses through electrolysis, liquefaction, fuel cell and electrical engine. The requirement of 15 hours operation on full load can be met if an input of 14.36 MW is granted for the same concept. However, due to the lower losses through compression, a 15 MW input can satisfy the demand for both 350 bar and 700 bar storage concepts.

Results show that assuming the concept with hydrogen combustion engines, the system efficiency can be at least 25%, which is higher than all the fuel cell configurations. The engine can provide 5.5 MW for more than 16 hours in operation if 15 MW input is assumed. Considering hydrogen storage in compressed form at 350 bar and a hydrogen direct injection engine, the system efficiency can be as high as 29%. The drawback of huge storage capacities for compressed hydrogen must be considered though.

4.4. Analysis of Methanol

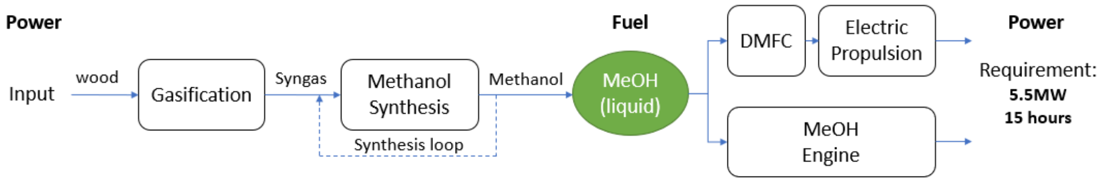


Figure 30: Block diagram methanol processes (Source: Own design).

The analysis of methanol is based on a study by Morandin and Harvey (2015), who modelled a methanol production site based on wood feedstock. The approach is different compared to the ammonia and hydrogen concepts because there is no electrolyser used and no initial base case assumed for the calculation of efficiencies.

Thus, the calculation steps start with the output requirements which are again assumed as 5.5 MW propulsion power and 15 hours duration running. In Table 14, the conversion of MeOH-to-Power is described, assuming 0.8 litre per kWh fuel consumption of the direct methanol fuel cell. It uses a mixture of 60% methanol and 40% water based on the numbers provided by SerEnergy (2018). Including a 5% loss in the electrical engine, the power output of the DMFC must be 5.79 MW to satisfy the propulsion requirements. The resulting fuel mixture consumption is 2,779 litre per hour.

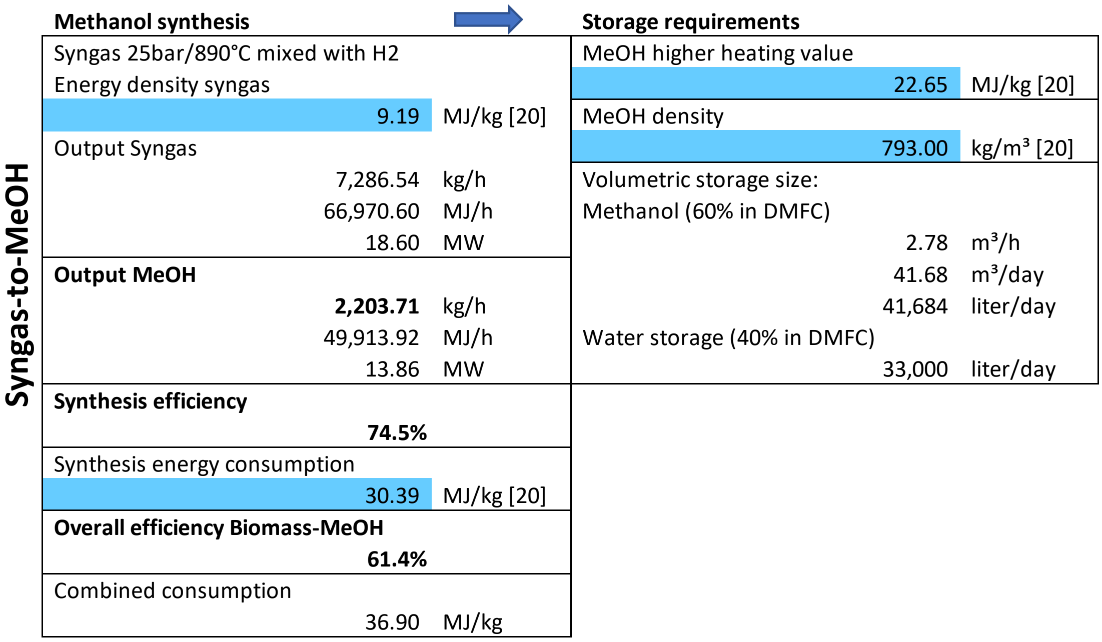
MeOH-to-Power

Direct Methanol Fuel Cell (DMFC) → Propulsion			**Internal Combustion Engine (ICE)** → Propulsion		
Energy consumption DMFC based on 30 kW PEM/MeOH Reformer [16]	0.80	litre/kWh	Energy consumption ICE: Specific fuel consumption	0.49	litre/kWh
Pure methanol consumption	0.48	litre/kWh			
Fuel consumption (60% MeOH)	2,203.71	kg/h	Fuel consumption (100% MeOH)	2,137.34	kg/h
	2,778.95	litre/h		**2,695.26**	litre/h
	41,684.21	litre/day		41,684.21	litre/day
Energy content	13,864.98	kW	Energy required for propulsion	13,447.43	kW
	207,974.68	kWh		207,974.68	kWh
Specific requirement for propulsion	9.46	MJ/kg	Specific requirement for propulsion	9.26	MJ/kg
Energy efficiency DMFC (excluding propulsion)	**41.8%**		**Energy efficiency ICE**	**40.9%**	[21]
Round-trip-efficiency	**24.3%**		**Round-trip-efficiency**	**25.1%**	
Duration on full load DMFC	15.00	h	Duration on full load ICE	15.47	h
Output DMFC	5,789.47	kW	**Output Propulsion ICE**	5,500.00	kW
	20,842.11	MJ/h		19,800.00	MJ/h
Output Propulsion	5,500.00	kW			
	19,800.00	MJ/h			

Table 14: Methanol: Power-to-syngas [16] (SerEnergy, 2018); [21] (Haraldson and Wärtsilä, 2015).

Numbers provided for the internal combustion engine are based on a manufacturer's report, indicating an efficiency of 40.9% for a marine engine running on methanol (Haraldson and Wärtsilä, 2015). The consumption of fuel, which is 100% methanol, results in almost 2,700 litres per hour, delivering a power output of 5.5 MW. It must be considered that the fuel cell has a power output of 5.79 MW to cover the losses of the electric propulsion, hence, the specific fuel consumption per kWh output is lower compared to the combustion engine. In accordance, the efficiency of the methanol combustion engine is slightly lower indicated with 40.9% compared to 41.8% of the

DMFC. However, the running duration of the combustion engine is longer due to the lower absolute consumption. In order to feed the propulsion, the methanol synthesis must produce the required amount of 41,684 litres per day which is equivalent to almost 208 MWh. The storage capacity required for the energy used every day is estimated with 41.68m³, which is significantly less than the requirements for liquid ammonia or hydrogen storage. This is because the propulsion efficiency of both the methanol engine and the DMFC is higher compared to the SOFC or the PEMFC.



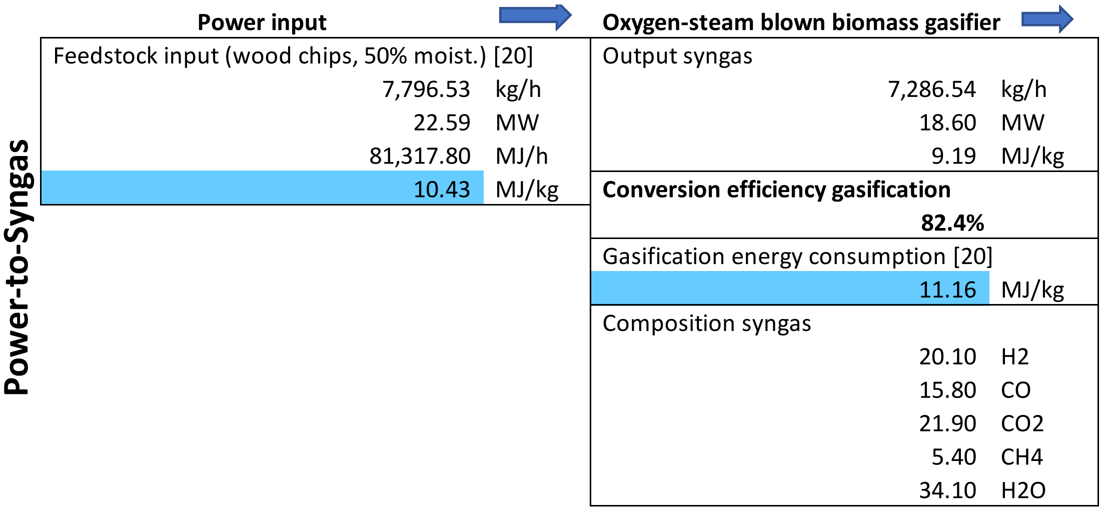
Syngas-to-MeOH

Methanol synthesis		
Syngas 25bar/890°C mixed with H2		
Energy density syngas		
	9.19	MJ/kg [20]
Output Syngas		
	7,286.54	kg/h
	66,970.60	MJ/h
	18.60	MW
Output MeOH		
	2,203.71	kg/h
	49,913.92	MJ/h
	13.86	MW
Synthesis efficiency		
	74.5%	
Synthesis energy consumption		
	30.39	MJ/kg [20]
Overall efficiency Biomass-MeOH		
	61.4%	
Combined consumption		
	36.90	MJ/kg

Storage requirements		
MeOH higher heating value		
	22.65	MJ/kg [20]
MeOH density		
	793.00	kg/m³ [20]
Volumetric storage size:		
Methanol (60% in DMFC)		
	2.78	m³/h
	41.68	m³/day
	41,684	liter/day
Water storage (40% in DMFC)		
	33,000	liter/day

Table 15: Methanol: Syngas-to-Methanol [20] (Morandin and Harvey, 2015).

In the first place, the methanol production requires the gasification of biomass to form syngas. Afterwards, it can be used for the methanol synthesis loop. Assuming an energy consumption of 30.39 MJ/kg, the methanol synthesis can achieve a conversion efficiency of 74.5% (Morandin and Harvey, 2015). This consumption requires an input of 7,286 kg of syngas with an assumed energy density of 9.19 MJ/kg (*ibid*). Further, the gasification process for the syngas production requires 11.19 MJ/kg resulting in 7,797 kg of biomass input under the assumption of 10.43 MJ/kg higher heating value for wood chips with 50% moisture content.



	Power input		**Oxygen-steam blown biomass gasifier**	
Power-to-Syngas	Feedstock input (wood chips, 50% moist.) [20]		Output syngas	
	7,796.53	kg/h	7,286.54	kg/h
	22.59	MW	18.60	MW
	81,317.80	MJ/h	9.19	MJ/kg
	10.43	MJ/kg	**Conversion efficiency gasification**	
			82.4%	
			Gasification energy consumption [20]	
			11.16	MJ/kg
			Composition syngas	
			20.10	H2
			15.80	CO
			21.90	CO2
			5.40	CH4
			34.10	H2O

Table 16: Methanol: Methanol-to-Power [20] (Morandin and Harvey, 2015).

After all, a total input of 22.59 MW of biomass or the amount of 339 MWh every day, is required to deliver enough methanol fuel to power the ferry for 15 hours on its daily route. The overall efficiency of the fuel cell and the internal combustion engine is quite comparable. The gains of a slightly more efficient fuel cell are cancelled out by the additional losses through the electric propulsion.

5. Discussion

5.1. Efficiency and Fuel Economy

In Chapter 4 the results of three of the most promising fuels for shipping are described in detail with each of the conversion steps required. In this section, the efficiencies of all the different concepts are once more investigated in a broader scope. Figure 31 represents graphically the different processes for the fuel production. On the left-hand side, symbols indicate the required feedstock for the process, whereas, on the right-hand side, the power-to-fuel efficiency indicates the losses through the production process.

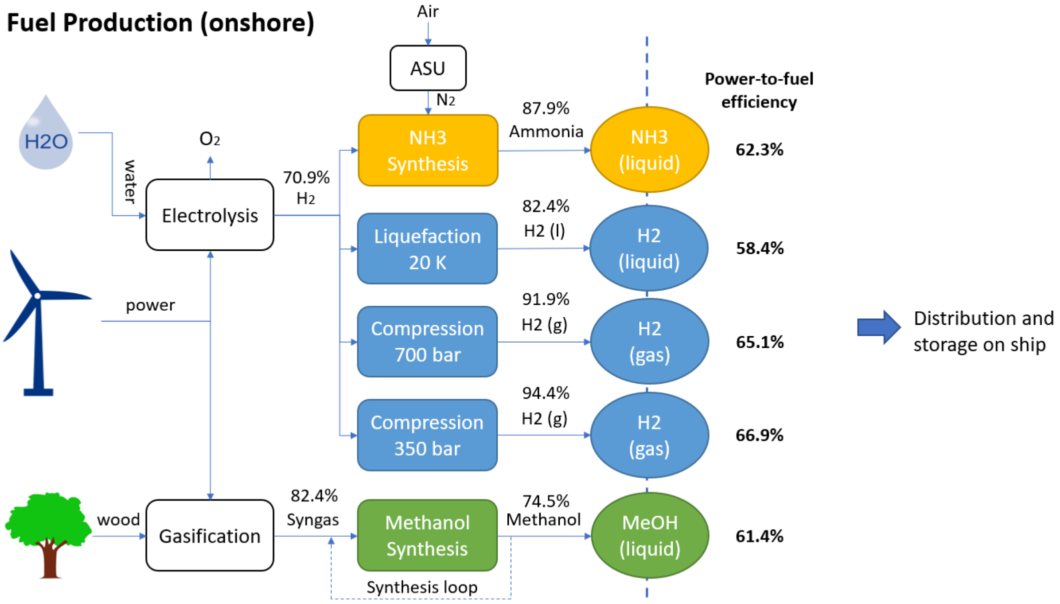


Figure 31: Overview of power to fuel efficiencies (Source: Own design).

The electrolysis is the initial step for both the ammonia production and the hydrogen production, with the difference that hydrogen does not need to be further converted to another substance, but work is required to store hydrogen at a reasonable energy density. To put numbers in words, the liquefaction of hydrogen into its most dense form requires more energy than the conversion of hydrogen into ammonia.

Although the ammonia synthesis efficiency also includes the air separation unit, the power demand of the Haber-Bosch process is lower compared to the cooling of hydrogen to a liquid state. Moreover, the storage and distribution of cryogenic fuels is sophisticated and only applied in specific industries, but not on a large scale and much less in shipping.

It is more practical and more efficient to store hydrogen in compressed form. However, the energy density is with 4.7 GJ/m³ significantly lower compared to 8.5 GJ/m³ in a liquid state. Only considering the power-to-fuel efficiency, the best solution with the least energy losses is the compression of hydrogen to 350 bar. Liquid hydrogen though has the worst power-to-fuel efficiency of all and requires the most advanced storage and distribution infrastructure. Therefore, liquid hydrogen can be already excluded as a proposed solution for a ferry service.

However, there are still other key figures to consider. The performance of the conversion from fuel-to-power shows slightly different results (see Figure 32). Each of the chosen fuels can be either processed in a fuel cell or in a combustion engine, resulting in six different propulsion systems with different efficiencies.

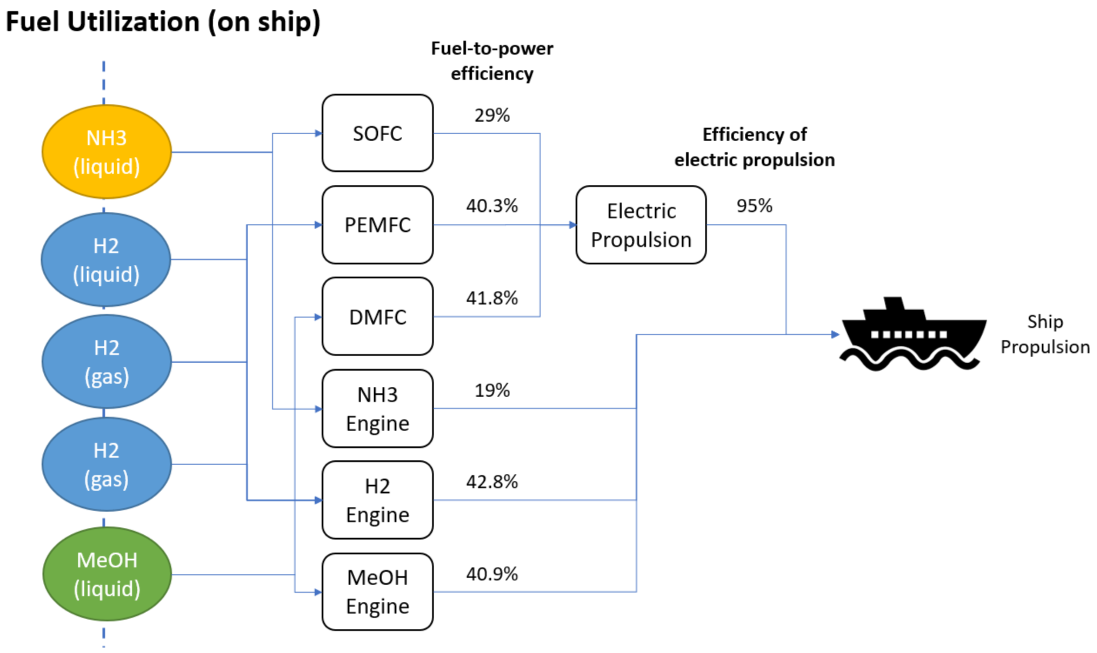


Figure 32: Overview of fuel to power efficiencies (Source: Own design).

Whereas internal combustion engines deliver mechanical power directly to the propeller shaft, fuel cells need an electric motor to drive the propeller. The losses in electric engines can be assumed with 5%. Even if the additional component adds losses to the system, the performance can still compete with conventional propulsion types and some concepts can even exceed them.

The combined efficiency of power-to-fuel, fuel-to-power and in the case of fuel cells, also of the electric engine, is represented in Table 17. In case of ammonia, the fuel cell performs better compared to the combustion engine. This is primarily due to the poor combustion characteristics of ammonia in the engine based on the model by Kong (2008). Other types of ammonia fed engines with a higher rate of combustion promoters such as hydrogen or diesel can theoretically perform better. A reliable estimation cannot be made due to lacking practical tests of alternative fuels in combustion engines. Although various tests with different fuels in fuel cells have been conducted, estimations are still based on modules with much lower power outputs compared to the actually required ship propulsion power. Especially direct methanol fuel cells have not been applied in a multi-megawatt scale so far and fuel consumption is just scaled up linearly.

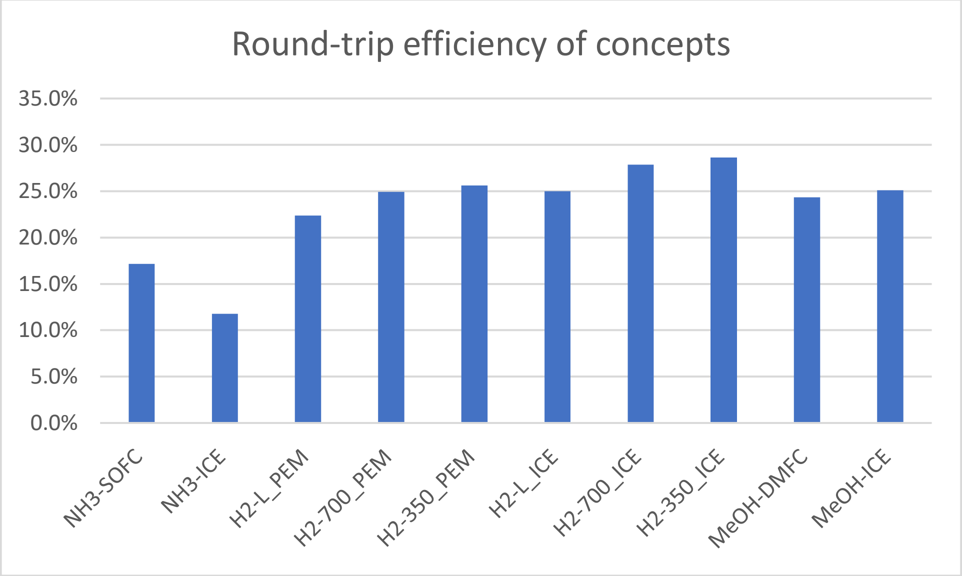


Table 17: Overview of round-trip-efficiencies (Source: Own design).

Having a look at the bars in Table 17, the round-trip-efficiencies of the investigated concepts can be compared. Equal to the lowest conversion efficiency of power-to-fuel, also the round-trip-efficiency is best for hydrogen compressed to 350 bars, achieving 28.6% efficiency. The other hydrogen concepts are in a range between 22-28%. Methanol as a fuel performs similarly with 24.3% in the combustion engine and 25.1%

in the DMFC. Unfortunately, ammonia cannot compete in terms of efficiency. Even if the conversion from power to fuel is competitive with other concepts, the losses in both the combustion engine and the fuel cell are significantly higher. The round-trip-efficiency is clearly below 20%, which disqualifies ammonia from other fuels. Only considering the fuel economy, the approach of methanol or compressed hydrogen appears to be the preferred one.

5.2. Storage Capacity

As described in Chapter 4, hydrogen at 350 bar needs a lot of space due to its low volumetric density. In fact, to store the same amount of energy, the tank for hydrogen under 350 bars must be more than 6 times larger compared to a methanol tank and even 11 times larger compared to a tank with diesel. The bars in Table 18 illustrate the storage requirements in cubic metres to meet the demand of the modelled ship with a 5.5 MW propulsion for 15 hours. All the losses for the production and the utilisation of the fuel are included. It appears that conversion efficiencies and storage capacity are disadvantageous to each other because the two best concepts in terms of efficiency have the worst energy per volume ratio. On the contrary, the concepts with the smallest storage capacity such as methanol or ammonia have poor efficiencies.

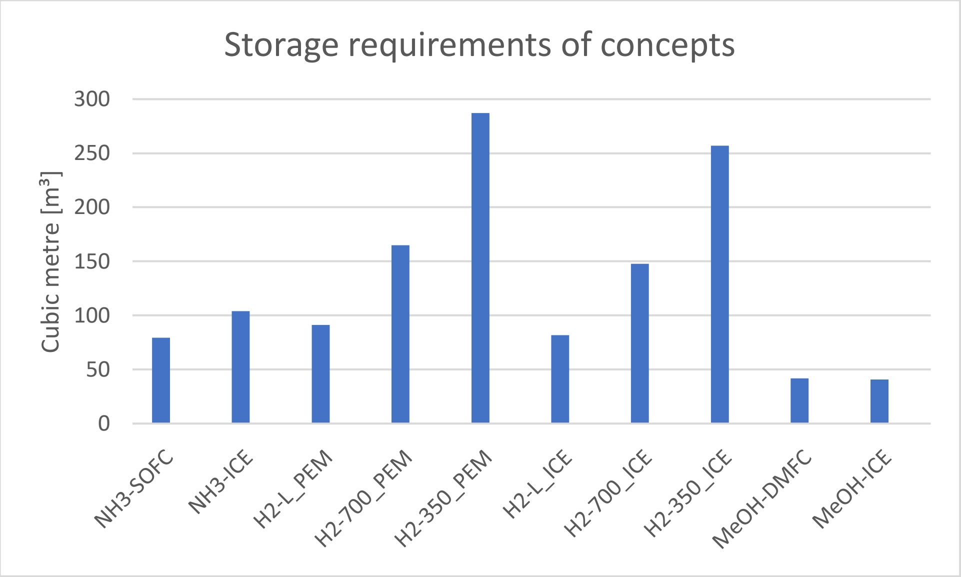


Table 18: Overview of storage requirements (Source: Own design).

Even storing hydrogen at 700 bar requires significantly more space compared to liquid fuels. Liquid hydrogen only needs half of the size of a tank to store the same amount of energy. Methanol only requires 43m^3 to contain enough energy to power the ship for 15 hours on full load, while the tank for compressed hydrogen at 700 bar must be around 164m^3 in volume. Ammonia is quite in the middle and, in the case of the better performing SOFC, the tank size must be around 80m^3. However, ammonia in a liquid state needs to be compressed to 10 bars, which makes the storage slightly more challenging compared to methanol tanks.

At this point, the space requirements for the facilities on board must be mentioned as well. The space needed for internal combustion engines running on alternative fuels is hardly different to engines running on conventional fuels. However, fuel cells have not been built at such a scale on ships before. According to one of the leading fuel cell manufacturers, the space requirements for a 1 MW PEMFC module is indicated as in Table 19.

Weight and space requirements of PEM fuel cell		
Specific numbers per module		
	40,000.00	kg/Mwe [8]
	2.9x2.4x9x2	m/Mwe [8]
Total weight		
	231,578.95	kg
Total space		
	725.31	m^3
Total area		
	250.11	m^2

Table 19: Weight and space requirements PEMFC [8] (Balllard, 2012).

The total space and area required for a 5.5 MW fuel cell are 725m^3 and 250m^2 respectively. An electrical propulsion unit must be added though. Unfortunately, there are no specific data available about the electrical propulsion unit or any other fuel cell type of this scale. Considering the size of the ship, space and weight requirements coming along with a fuel cell system are considered as feasible and not equally challenging compared to conventional propulsion concepts.

5.3. Environmental Impact

After all, the environmental impact has not been discussed so far but must be considered to support key benefits compared to conventional propulsion systems. Table 20 lists the current main emissions of the vessel “MV Clansman” in operation on the investigated route from Oban to Castlebay. The emissions are related to the annual fuel consumption based on data from the “Scottish Government Ferry Review” of 2010 (Table 20). Following paragraphs, shortly review and discuss some main points regarding the environmental impact.

Emissions MV Clansman	
	Diesel tons/year
Fuel consumption	5,841
CO2	19,305
NOx	446
Sox	< 29

Table 20: Emissions of modelled vessel (Caledonian Maritime Assets Ltd, 2010).

Ammonia

In this report, the emissions from ammonia production and utilisation are neglected. The reason for that is the absence of any carbon atoms in the ammonia molecule, resulting in a carbon-free life cycle. However, it is assumed that the production is exclusively based on electrolysis and non-fossil fuels. Basically, nitrogen oxides can still occur during the combustion or decomposition of ammonia, but this can be controlled by keeping temperatures on an acceptable low level. A study of the American Chemical Society, reports that at 600°C a complete decomposition of ammonia into hydrogen and nitrogen can be achieved without any considerable NOx emissions (Giddey, et al., 2017). According to Kong (2008), the NOx formation during the combustion of ammonia-diesel mixtures remains below conventional diesel fuel, while unburnt ammonia remains a bigger issue due to poor flame propagation. Nevertheless, unburnt ammonia is not considered as a GHG and is biodegradable. The impact to humans though must be taken seriously and any leakage of ammonia must be avoided. The fact that ammonia disappears quickly reduces safety concerns just as the narrow flammability limits. In terms of environmental impact and safety issues, ammonia appears to be a suitable fuel with controllable emissions and manageable safety precautions.

Hydrogen

Hydrogen itself is the cleanest and purest fuel with an enormous energy content per mass. Even if hydrogen is the most abundant element in the universe, it exists very rarely in its pure form of the diatomic molecule H2. Therefore, some energy is needed to produce hydrogen and if the energy used is not based on renewable resources, the carbon footprint is also remarkable. However, in this study, only hydrogen production from renewable electricity is considered. The feedstock for the electrolysis is limited to water and electrical energy to split the H2O molecule into H2 and O2 (see Figure 10). There are no direct GHG emissions at all, even if diatomic hydrogen supports the formation of hydroxyl radicals which prevents the degradation of other GHGs. Further, this only occurs if the combustion in hydrogen engines or the conversion in fuel cells is incomplete. The feedstock requirements of around 20 litres of water per produced kg hydrogen must be considered and its availability at potential locations for electrolysers ensured.

Methanol

Unlike the other investigated fuels, methanol contains carbon in its molecule which is about 38% of its mass (Andersson and Salazar, 2015). Even if it is only half of the mass fraction of conventional fuels, it must be considered and both the production as well as the utilisation carefully adapted. Just like ammonia, the conventional production of methanol is primarily based on natural gas or coal. However, in this report, only the production based on wood chips is considered. Thus, the carbon cycle can be closed because the release of carbon during combustion is equal to the amount absorbed from plants during their life cycle. Unfortunately, to achieve the correct syngas composition during the biomass gasification, not all of the CO2 can be used and is released to the environment. According to Martin and Grossman (2017), at least 0.675 kg of CO2 is released per kilogram of produced methanol. Capturing the CO2 and reusing it in a synthesis loop with additional hydrogen supply, can enhance the methanol production and reduce CO2 emissions towards zero (Martin and Grossmann, 2017).

The utilisation of methanol either through fuel cells or combustion engines releases CO2 naturally due to its carbon content. However, the emissions are significantly lower compared to diesel fuel. The Swedish ferry company Stena Line claimed that their 24 MW ship Stena Germanica could reduce its CO2 emissions by 25%. Moreover, a reduction of sulphur oxide by 99%, particles by 95% and nitrogen oxide by 60% has been measured (Stena Line, 2015).

The following table compares the emission values of the "MV Clansman" running on diesel and estimated emission values running on methanol, based on the provided data by Stena Line.

Estimated emissions MV Clansman running on methanol		
	Diesel tons/year	Methanol tons/year
Fuel consumption	5,841	11,542
CO2	19,305	14,479
NOx	446	146
SOx	< 29	<0.3

Table 21: Estimated emissions from methanol (Source: Own design).

6. Conclusion

The investigation of ammonia, hydrogen and methanol as proposed fuels for a Scottish ferry service, are chosen because of their extraordinary properties as fuels, their applicability in vessels and their low environmental impacts. These fuels are well known in the industry and for the implementation in transport sector suitable. Moreover, the chosen fuels stand out by their high volumetric energy density which is a crucial factor for space limited vessels with proper range requirements. The results of the tool have delivered some valuable but also surprisingly outputs for the validation of the best suitable fuel.

First and foremost, the conversion efficiencies in fuel cells are hardly better compared to internal combustion engines. This might be due to the fact, that internal combustion engines running on alternative fuels are mainly tested in laboratories and are not quite comparable to the numbers in a real application. Research for fuel cells has also shown very volatile test results, depending on many circumstances which cannot be estimated accurately for application in multi-megawatt vessels. However, careful investigations have resulted in the disqualification of some fuel concepts due to individual reasons.

Ammonia has shown very poor efficiency with values that are hardly competitive to hydrogen or methanol. Primarily because of its narrow flammability limits and low flame speed, ammonia has a poor combustion behaviour in internal combustion engines. It would make more sense to use ammonia together with a combustion promoter such as hydrogen or diesel. SOFCs have shown poor efficiencies due to the high-temperature decomposition of ammonia into hydrogen and nitrogen, but also due to the limiting temperature factor of NOx formation. Even if ammonia was initially assumed as the fuel with the greatest potential it cannot be recommended as the best suitable fuel for shipping.

Hydrogen has shown some good results in terms of efficiency but bad results in terms of storage requirements. A massive amount of high-pressure storage tanks would be needed to meet the demand of the ship for 15 hours and a 5.5 MW load. However, the conversion efficiency and process complexity are very advantageous compared to ammonia or methanol. Moreover, PEMFCs are most experienced and easiest purchasable in a multi-megawatt scale. The application of internal combustion engines running on hydrogen shows a good performance as well, but with minor experience and the disadvantage of pre-ignition issues and sophisticated operation.

Methanol seems to be the best solution in terms of storage capacity, but also good efficiency values compared to the other investigated options. The complex production process and the release of carbon emissions as well as nitrogen oxides must be considered though. Even if DMFCs are well experienced, they have only been used in small applications up to a few hundred kilowatts. Reliability is also a limiting factor because of its sensitivity to impurities. However, internal combustion engines using methanol are successfully in operation and only minor changes are necessary to run conventional marine engines on methanol. Nevertheless, higher fuel consumption and cautious handling of methanol must be considered.

As a final proposal, the use of methanol as a ship fuel can be recommended since it is the most advanced concept and the easiest to implement. Good local conditions and availability of renewable resources are obligatory. Even if reductions in emissions can be expected, it is not a carbon-free solution as it might be favoured. In case of a preferred carbon-free solution, the best concept might be the usage of highly compressed hydrogen at 700 bar with the drawback of larger storage tank requirements. Apart from that, hydrogen is the cleanest option with more and more experienced conversion processes, good efficiencies and a good chance for further applications in shipping.

As a final statement it must be mentioned that the calculations in the tool are based on research results and may not be accurate in real applications.

7. Further Work

The scope in this work is limited to a technical review including the investigation of different fuels for its applicability in shipping. It does not include any economic considerations which must be considered for a more detailed concept proposal.

The approach of using gas turbines instead of internal combustion engines has not been considered, because initial research has shown that the applicability of alternative fuels such as ammonia or methanol is even worse in turbines. However, especially for larger ships and ocean-going vessels gas turbines must be implied and the applicability of hydrogen or even other fuels based on renewable resources further investigated.

Another related but disregarded field is the applicability of batteries in shipping. Even if batteries also deal with the issue of large space requirements and low energy per volume density, they must be considered in further studies, especially for short distance ferries.

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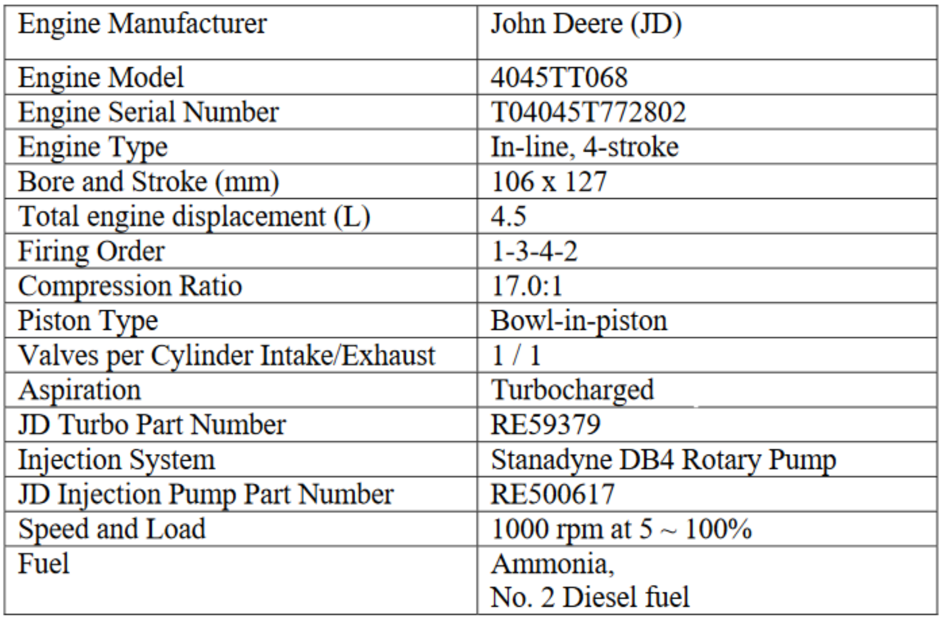
List of Appendices

Appendices

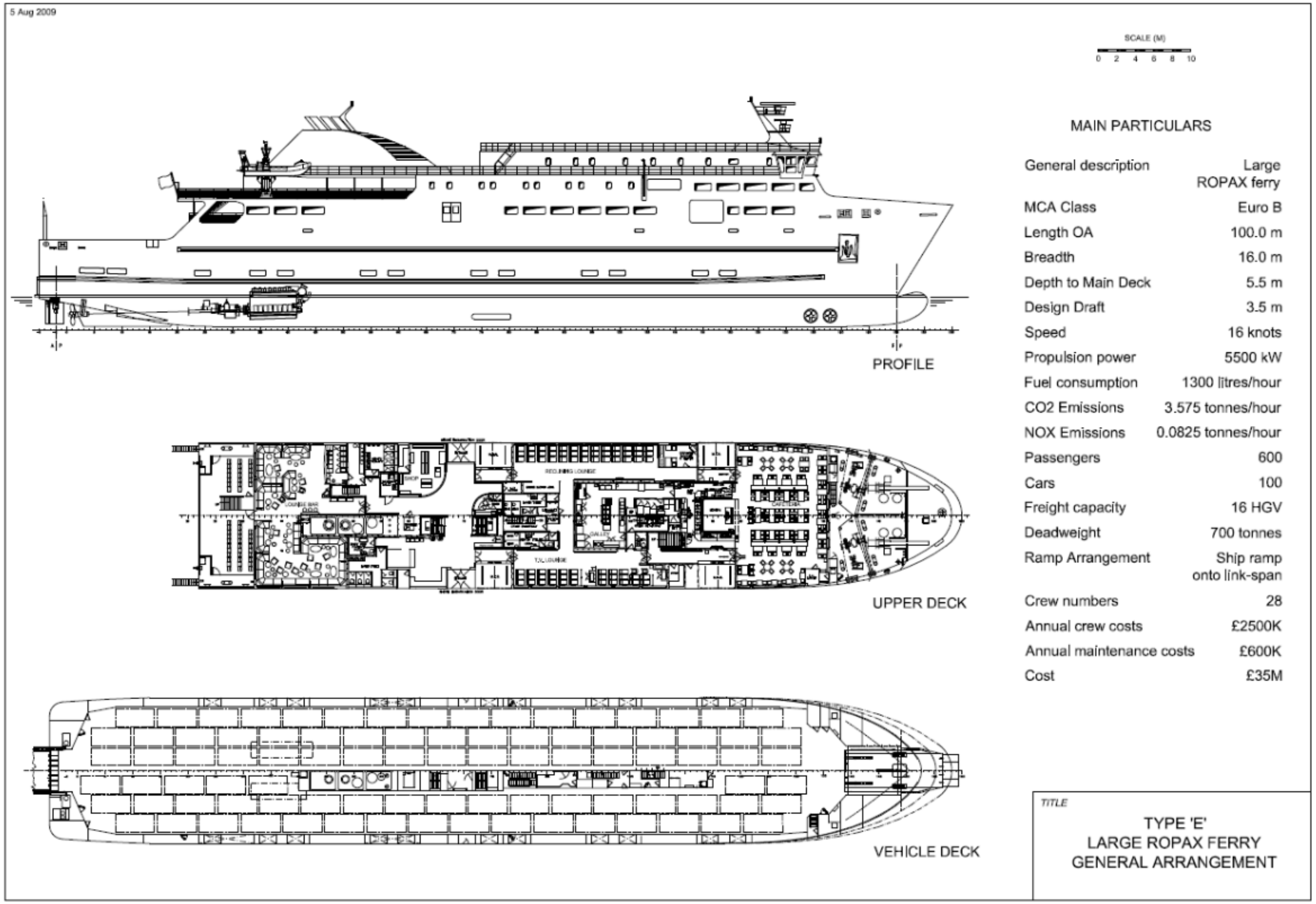
Appendix A: Diesel-Ammonia Dual Fuel Test Engine



Engine Manufacturer	John Deere (JD)
Engine Model	4045TT068
Engine Serial Number	T04045T772802
Engine Type	In-line, 4-stroke
Bore and Stroke (mm)	106 x 127
Total engine displacement (L)	4.5
Firing Order	1-3-4-2
Compression Ratio	17.0:1
Piston Type	Bowl-in-piston
Valves per Cylinder Intake/Exhaust	1 / 1
Aspiration	Turbocharged
JD Turbo Part Number	RE59379
Injection System	Stanadyne DB4 Rotary Pump
JD Injection Pump Part Number	RE500617
Speed and Load	1000 rpm at 5 ~ 100%
Fuel	Ammonia, No. 2 Diesel fuel

Source: Kong (2008).

Appendix B: ROPAX Ferry

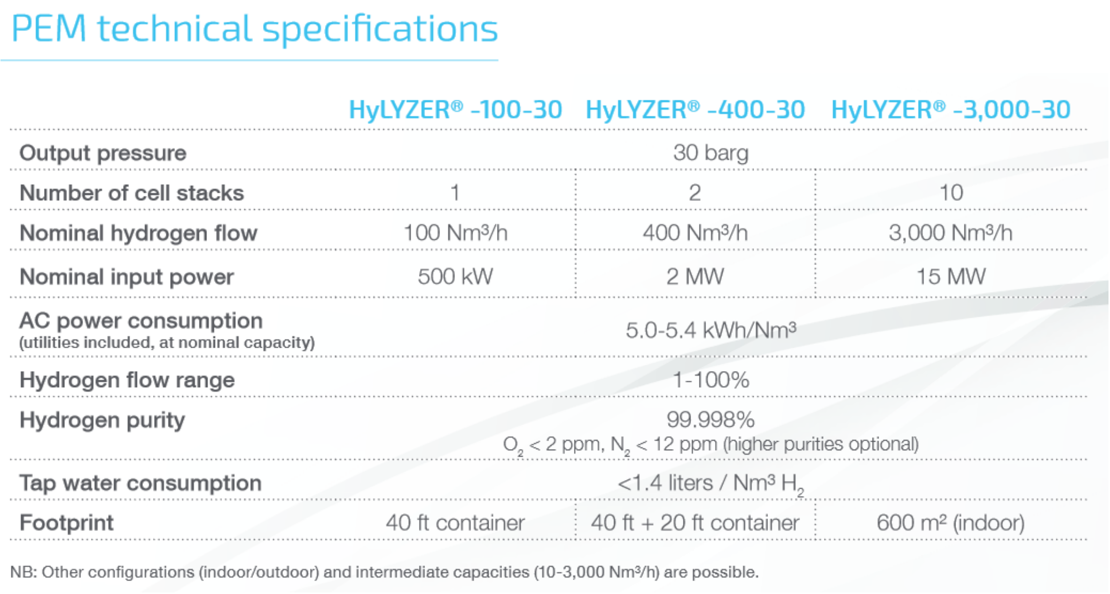


MAIN PARTICULARS

General description	Large ROPAX ferry
MCA Class	Euro B
Length OA	100.0 m
Breadth	16.0 m
Depth to Main Deck	5.5 m
Design Draft	3.5 m
Speed	16 knots
Propulsion power	5500 kW
Fuel consumption	1300 litres/hour
CO2 Emissions	3.575 tonnes/hour
NOX Emissions	0.0825 tonnes/hour
Passengers	600
Cars	100
Freight capacity	16 HGV
Deadweight	700 tonnes
Ramp Arrangement	Ship ramp onto link-span
Crew numbers	28
Annual crew costs	£2500K
Annual maintenance costs	£600K
Cost	£35M

Source: Caledonian Maritime Assets Ltd (2010).

Appendix C: PEM Technical Specifications



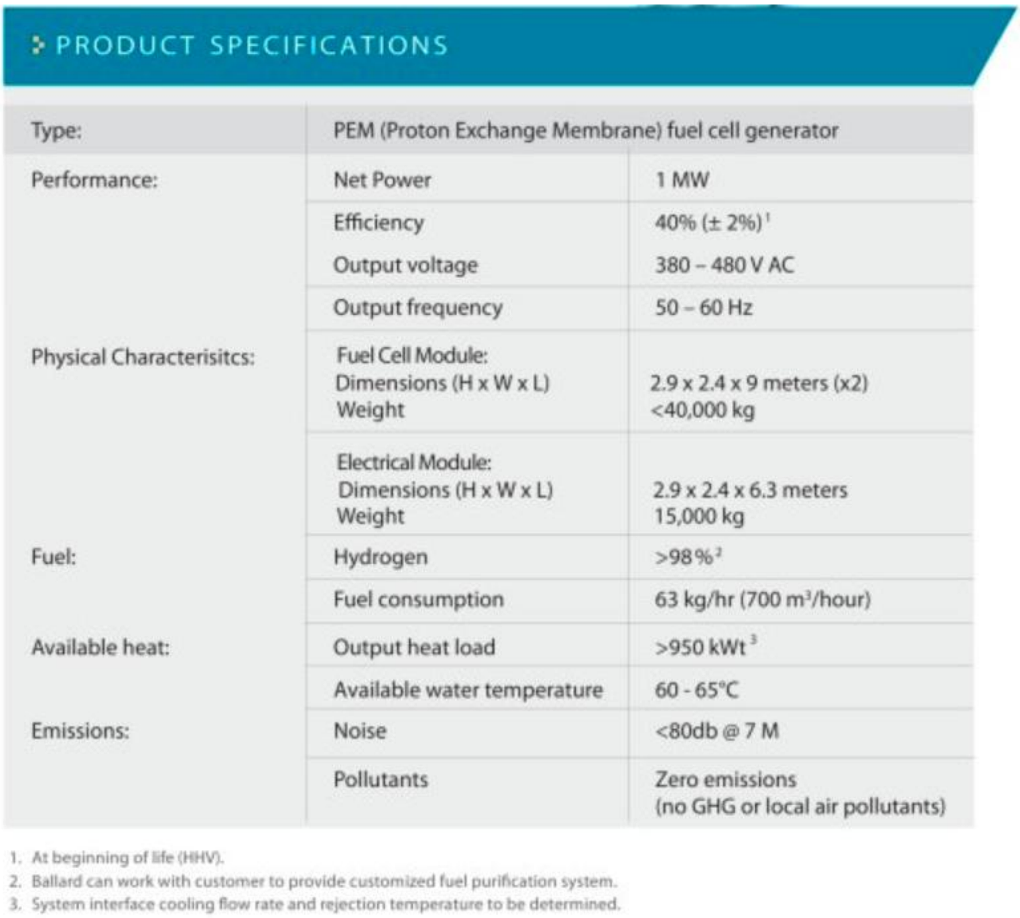
PEM technical specifications

	HyLYZER® -100-30	HyLYZER® -400-30	HyLYZER® -3,000-30
Output pressure	30 barg		
Number of cell stacks	1	2	10
Nominal hydrogen flow	100 Nm^3/h	400 Nm^3/h	3,000 Nm^3/h
Nominal input power	500 kW	2 MW	15 MW
AC power consumption (utilities included, at nominal capacity)	5.0-5.4 kWh/Nm^3		
Hydrogen flow range	1-100%		
Hydrogen purity	99.998% O_2 < 2 ppm, N_2 < 12 ppm (higher purities optional)		
Tap water consumption	<1.4 liters / Nm^3 H_2		
Footprint	40 ft container	40 ft + 20 ft container	600 m^2 (indoor)

NB: Other configurations (indoor/outdoor) and intermediate capacities (10-3,000 Nm^3/h) are possible.

Source: Hydrogenics (2016).

Appendix D: Product Specifications



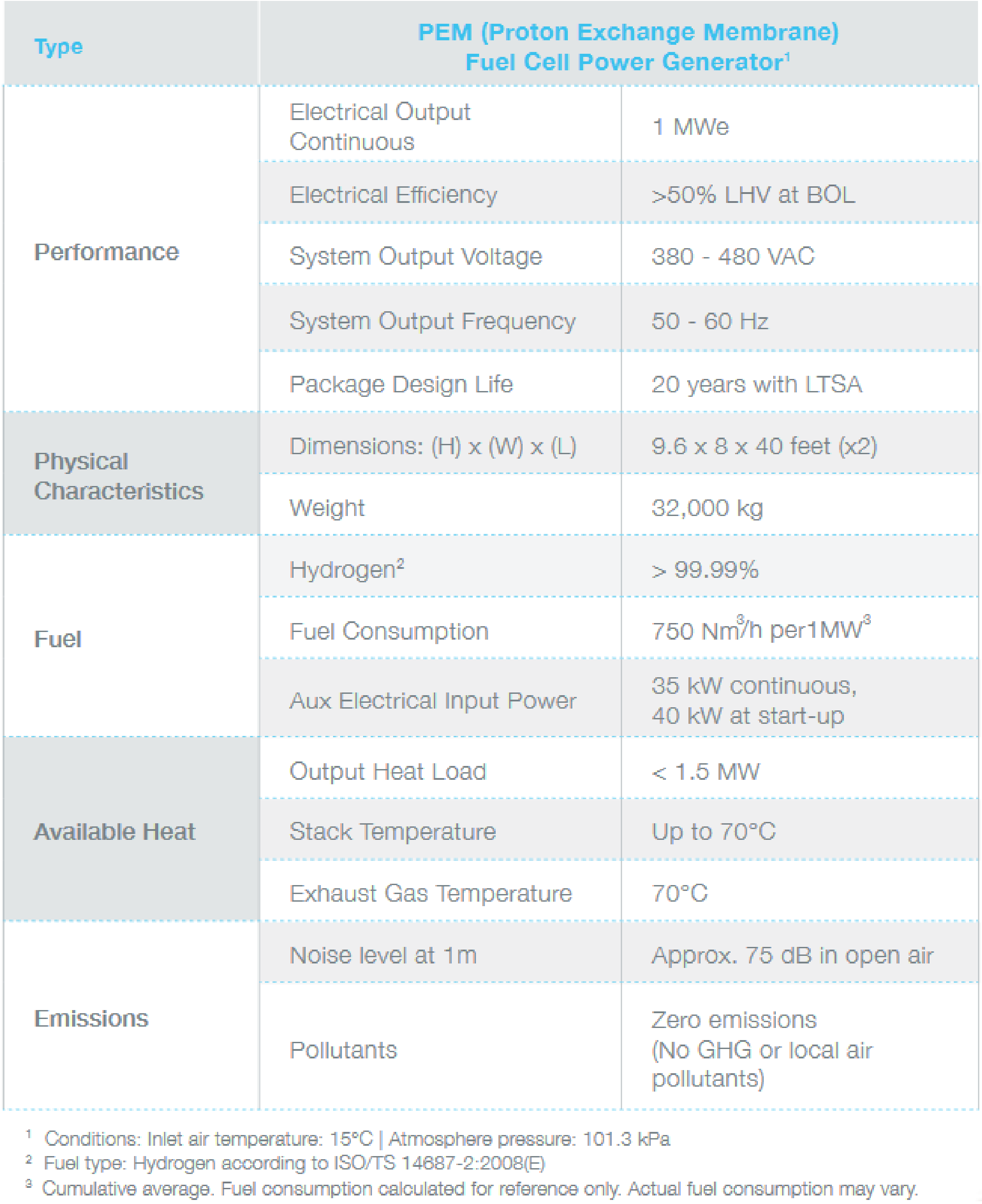
PRODUCT SPECIFICATIONS

Type:	PEM (Proton Exchange Membrane) fuel cell generator	
Performance:	Net Power	1 MW
	Efficiency	40% (± 2%)[1]
	Output voltage	380 – 480 V AC
	Output frequency	50 – 60 Hz
Physical Characterisitcs:	Fuel Cell Module:	
	Dimensions (H x W x L)	2.9 x 2.4 x 9 meters (x2)
	Weight	<40,000 kg
	Electrical Module:	
	Dimensions (H x W x L)	2.9 x 2.4 x 6.3 meters
	Weight	15,000 kg
Fuel:	Hydrogen	>98%[2]
	Fuel consumption	63 kg/hr (700 m^3/hour)
Available heat:	Output heat load	>950 kWt[3]
	Available water temperature	60 - 65°C
Emissions:	Noise	<80db @ 7 M
	Pollutants	Zero emissions (no GHG or local air pollutants)

1. At beginning of life (HHV).
2. Ballard can work with customer to provide customized fuel purification system.
3. System interface cooling flow rate and rejection temperature to be determined.

Source: Ballard (2012).

Appendix E: Proton Exchange Membrane



Type	PEM (Proton Exchange Membrane) Fuel Cell Power Generator[1]	
Performance	Electrical Output Continuous	1 MWe
	Electrical Efficiency	>50% LHV at BOL
	System Output Voltage	380 - 480 VAC
	System Output Frequency	50 - 60 Hz
	Package Design Life	20 years with LTSA
Physical Characteristics	Dimensions: (H) x (W) x (L)	9.6 x 8 x 40 feet (x2)
	Weight	32,000 kg
Fuel	Hydrogen[2]	> 99.99%
	Fuel Consumption	750 Nm^3/h per1MW[3]
	Aux Electrical Input Power	35 kW continuous, 40 kW at start-up
Available Heat	Output Heat Load	< 1.5 MW
	Stack Temperature	Up to 70°C
	Exhaust Gas Temperature	70°C
Emissions	Noise level at 1m	Approx. 75 dB in open air
	Pollutants	Zero emissions (No GHG or local air pollutants)

[1] Conditions: Inlet air temperature: 15°C | Atmosphere pressure: 101.3 kPa

[2] Fuel type: Hydrogen according to ISO/TS 14687-2:2008(E)

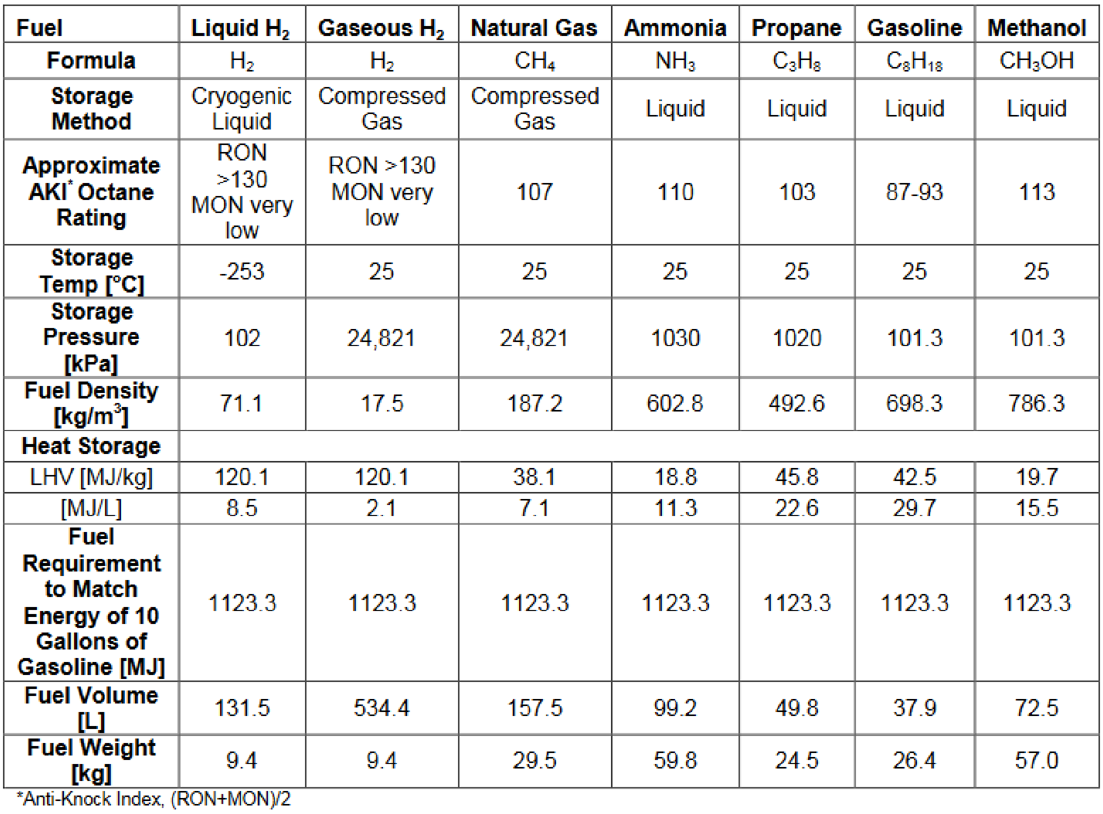
[3] Cumulative average. Fuel consumption calculated for reference only. Actual fuel consumption may vary.

Source: Hydrogenics (2018).

Appendix F: CALMAC Ferry Route

Source: CALMAC (2018).

Appendix G: Overview Fuel Properties



Fuel	Liquid H_2	Gaseous H_2	Natural Gas	Ammonia	Propane	Gasoline	Methanol
Formula	H_2	H_2	CH_4	NH_3	C_3H_8	C_8H_{18}	CH_3OH
Storage Method	Cryogenic Liquid	Compressed Gas	Compressed Gas	Liquid	Liquid	Liquid	Liquid
Approximate AKI* Octane Rating	RON >130 MON very low	RON >130 MON very low	107	110	103	87-93	113
Storage Temp [°C]	-253	25	25	25	25	25	25
Storage Pressure [kPa]	102	24,821	24,821	1030	1020	101.3	101.3
Fuel Density [kg/m^3]	71.1	17.5	187.2	602.8	492.6	698.3	786.3
Heat Storage							
LHV [MJ/kg]	120.1	120.1	38.1	18.8	45.8	42.5	19.7
[MJ/L]	8.5	2.1	7.1	11.3	22.6	29.7	15.5
Fuel Requirement to Match Energy of 10 Gallons of Gasoline [MJ]	1123.3	1123.3	1123.3	1123.3	1123.3	1123.3	1123.3
Fuel Volume [L]	131.5	534.4	157.5	99.2	49.8	37.9	72.5
Fuel Weight [kg]	9.4	9.4	29.5	59.8	24.5	26.4	57.0

*Anti-Knock Index, (RON+MON)/2

Source: Reiter (2009).