Maritime application of sodium borohydride as an energy carrier

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by

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Preface

This report presents the master thesis on maritime applications of sodium borohydride as an energy carrier performed by Floris van Nievelt. This thesis is executed at the marine engineering department of Delft, University of Technology.

During my study in maritime engineering I became truly inspired by the technical systems that makes the operations on-board of vessel possible. Especially the environmental impact of this systems and the various opportunities to decrease harmful emissions motivated me to start this project.

The use of hydrogen as a fuel has a high potential to decrease the harmful emissions in the maritime industry. This technology is, however, very young and encounters many challenges, such as the high volume and safety issues of this fuel. By using a material-based hydrogen storage, such as sodium borohydride, these challenges might be overcome. In this research the technical feasibility of this fuel in the maritime field is studied.

A research is never accomplished by one person. Therefore, I like to thank some people who played an important role in realizing this master thesis. First of all, I would like to thank my supervisors at the TU Delft: Klaas Visser, assistant professor of Marine Engineering, and my daily supervisor Lindert van Biert. Without their enthusiasm, knowledge and feedback I wouldn't be able to obtain these results. I have always been motivated to study this subject thanks to their guidance on this project.

Secondly, I would like to thank all attendees of the 'H2Fuel Holding BV'. They provided me with much knowledge on this technology, and made it possible to study the more practical implementation aspects, together with multiple parties in the maritime industry. A special tanks goes to inventor G. Lugtigheid from H2Fuel who invested much time to make me understand all concepts and to provide me with the chemical knowledge on this technology.

Thereafter, I like to thank my friends and family who supported me during my thesis and helped me to improve my report. A special thanks to my roommate Gerben Dekker who always helped me to get a clear overview of my thesis and had a critical view on my results.

F. M. van Nievelt
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Summary

The interest in alternative fuels in the maritime sector is growing due to increasing concerns of the effect of harmful emissions. Hydrogen in combination with a fuel cell has a high potential to be a more environmental friendly solution than the commonly used fossil fuel systems. However, the use of hydrogen encounters problems looking at the fuel storage density, safety and the operating profile of a vessel. Hydrogen storage in a material, such as sodium borohydride, has the potential to overcome or mitigate these problems. However, little is known about the implementation of a sodium borohydride system on-board of a vessel.

The goal of this research is to provide an insight in the technical feasibility of this technology for the maritime industry. Therefore, the following research question will be answered:
How does a technical design of a power train using sodium borohydride as hydrogen storage material on-board of vessels perform in terms of power and energy density and in a transient load?
First, multiple design options are analysed followed by its performance on: volumetric density, gravimetric density and safety. Thereafter, the results are used for a case study on the sailing passenger vessel the 'Stad Amsterdam' and a model is made to test the behaviour of the system on a typical transient hotel load of the clipper.

There are three important elements in this system: the sodium borohydride, water and the spent-fuel. The hydrogen in sodium borohydride can be released in a reaction with water, resulting in a hydrogen gas and liquid spent-fuel. The spent-fuel is preserved on-board for recycling back to sodium borohydride on land. The energy and power density is determined using the weights and volumes of these elements and by comparing each component in the system with existing components on the market. Both the least, and most compact configurations are considered to determine the operating range of this technology. A model is made and measurements are done on the power demand of the 'Stad Amsterdam' to investigate the performance of the system on dynamic behaviour. The most slow components, such as the mix-chamber, fuel cell and the battery system, are dynamically modelled to identify the critical elements in the design.

Multiple types of configurations are investigated resulting in a wide range in system density. In the first configuration, all fuels are stored in separate tanks and all the water needed for the process is stored on-board. This results in a low volumetric energy and power density. To improve the density of the system multiple concepts are considered: a concentrated or dry fuel, a volume-exchange tank, on-board water generation and a filtered spent-fuel. Implementing these concepts results in a compact configuration which is more competitive with diesel systems and other alternative fuels.

The hydrogen buffer in the mix chamber, the fuel cell and the battery systems are the most important elements influencing the performance of the system in a transient load. A more constant behaviour can be expected by making use of multiple mix chambers. The safety on-board of the vessel still needs attention, especially around the places containing hydrogen gas and where hydrochloric acid is present.

It can be concluded that this technology has a high potential for many types of applications in the maritime industry. It will be technically feasible to implement such a system on-board of a vessel. The application is especially advantageous because water, required for the process, can be generated on-board. The harmful emissions in this industry can be decreased significantly using this system. Cost and safety of the system are a challenge and, therefore, further research has to be done to realise the implementation of these systems on-board of vessels.

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Nomenclature

Abbreviations

AC	Alternating Current
AFC	Alkaline Fuel cell
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
CCR	Centrale Commissie voor de Rijnvaart
CH2	Compressed Hydrogen at 700 bar
CSA	the Clipper the Stad Amsterdam
CSTR	Continuous-Stirred Tank Reactor
DBFC	Direct Borohydride Fuel Cell
DC	Direct Current
DOE	Departement Of Energy
DOH	Degree Of Hybridisation
EIGA	European Industrial Gasses Association
HFO	Heavy Fuel Oil
HHV	Higher Heating Value
HT-PEMFC	High Temperature Proton-Exchange Membrane Fuel Cell
IBC	Intermediate Bulk Container
IBC	International Bulk Chemical
ICE	Internal Combustion Engine
ICSC	International Chemical Safety Cards
IGC	Industrial Gases Council
IGF	International code of safety for ships using Gases or other low-flashpoint Fuels
IMDG	International Maritime Dangerous Goods
IMO	International Maritime Organisation
ISO	International Organisation for Standardization
LH2	Liquified Hydrogen
LNG	Liquid Natural Gas
LT-PEMFC	Low Temperature Proton-Exchange Membrane Fuel Cell
MCFC	Molten Carbonate Fuel Cell
MGO	Marine GasOil
MSDS	Material Safety Data Sheet
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Proton-Exchange Membrane Fuel Cell
SB	Sodium Borohydride
SOC	State Of Charge
SOFC	Solid Oxide Fuel Cell
SOLAS	Safety Of Life At Sea
TRL	Technology Readiness Level
UN	United Nations
UPW	Ultra Pure Water

Symbols

C	Part of the reactants not reacted yet (-)
c_{H_2}	Hydrogen composition (%)
C_{rated}	Energy stored in the battery (Ah)
$E_{H_2,out}$	Chemical energy out of the reactor (J)
$E_{NaBH_4,in}$	Chemical enrgy into the reactor (J)
F	Faraday constant ($Cmol^{-1}$)
I	Current (A)
I_{ref}	Reference current (A)
k	Reaction rate (s^{-1}) (for a first order reaction)
n	Number of half-lifes (-)
n	Number of mol (mol)
N	Ammount of molecules (mol)
N	Concentration of a chemical in a solution (mol)
N_c	Number of cells (-)
$n_{H_2,out}$	Hydrogen out of the reactor (mol)
$n_{H_2,in}$	Hydrogne into the reactor in the reactants (mol)
p	Pressure (Pa)
P	Power (W)
p	Period between the start of an injection until the time the reactor is emtied (s)
p_0	Atmosperic pressure (bar)
P_{eff}	Effective power density (W)
R	Gas constant ($J/(K \cdot mol)$)
T	Temperature (K)
t	Time (s)
$t_{1/2}$	Half-life (s)
U	Internal energy (J)
U_f	Fuel utalization (%)
V	Volume (m^3)
W_{eff}	Effective energy density (Wh)
wt. %	Weight percentage (%)
x	Additional water needed in the reactor (mol)
η	Efficiency (%)
η_{H_2}	Hydrogen generation efficiency (%)
$\eta_{reactor}$	Reactor efficiency (%)

Chemicals and fuel types

Co	Cobalt
CO_2	Carbon dioxide
Fuel 30	30 wt.% Sodium borohydride solution in water with 5 wt.% sodium hydroxide
Fuel 50	50 wt.% Sodium borohydride solution in water with 7.5 wt.% sodium hydroxide
Fuel 66	66 wt.% Sodium borohydride solution in water with 10 wt.% sodium hydroxide
H_2	Hydrogen
H_2O	Hydrogen dioxide (water)
HCL	Hydrochloric adic
MeOH	Methanol
$Na_2B_4O_7$	Borax
$NaBH_4$	Sodium borohydride
$NaBO_2$	Sodium metaborate
NaOH	Sodium hydroxide (stabilizer)
No_x	Nitrogen oxides
SO_x	Sulpher oxides

1

Introduction

There is a growing concern on the effect of harmful emissions in the world. Greenhouse gasses are leading to an increase of the global temperature and pollutants, such as sulphur oxides (SO_x) and nitrogen oxides (NO_x) have a health impact on humans and the environment. It is, therefore, an international agreed objective to keep the global temperature increase below 2 °C and to reduce other environmental impacts due to harmful emissions. The use of fossil fuels in the maritime industry contributes to these negative effects on the environment. Changes in this sector have to be made to decrease this impact and, therefore, research towards cleaner or more efficient solutions is required.

An alternative for fossil fuels is the use of renewable fuels, such as: ethanol, methanol and hydrogen. Hydrogen attracts much interest, because it is a highly abundant fuel which has the potential to reduce harmful emissions significantly. Hydrogen (H_2) is not highly abundant in its pure form and is mostly produced from natural gas or by electrolysis. Hydrogen gas is very light and is, therefore, very energy dense in weight. The high volume of the gas at ambient conditions is, however, more problematic for the implementation on-board of vessels. Multiple methods are known to store the hydrogen in more compact way, as is illustrated in Figure 1.1.

In the first physical based method hydrogen is compressed to typical values of 350 and 700 bar. The volume decreases significant by pressurising the hydrogen gas, but it still suffers under a high volume in comparison with fossil fuels. Furthermore, heavy and volumetric tanks are required to secure the safety, resulting in a much lower gravimetric and volumetric energy density.

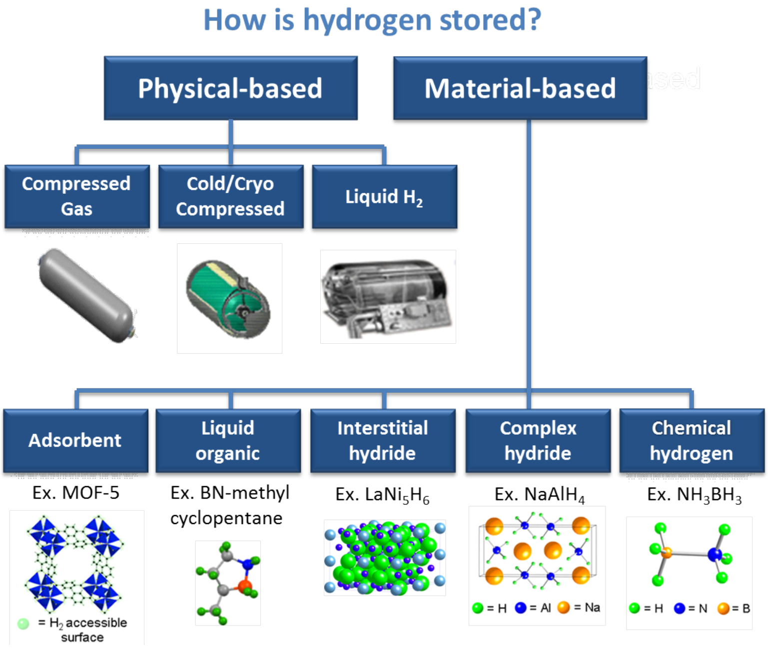

Figure 1.1: Hydrogen storage methods [3]

The second physical based method is the liquefaction of hydrogen, where the hydrogen is cooled down to a temperature of -253 °C. This method results in a more compact fuel than the compressed gas, but the volume remains an issue. Moreover, the weight, cost and volume of the tanks are high in comparison to conventional fuels such as marine gasoil (MGO) and heavy fuel oil (HFO). To liquefy the hydrogen a large amount of energy is required and since the boiling point is -253 °C, gasses are involving in the tanks (Boil-off gasses). This phenomenon makes the design of such a system more complicated, because of the pressure rise in the tanks [35].

In the material-based storage method the hydrogen is absorbed or bound to a material and released from the material in a chemical reactor or sometimes directly in a fuel cell. Many research has been performed towards these materials, because of the potential to store the hydrogen in a more compact way. Examples of commonly examined materials are: ammonia borane, different types of metal hydrides and adsorbent materials, mostly at lower temperatures [3]. An overview of multiple hydrogen storage materials is illustrated in Figure 1.2. The targets in the figure are based on the automotive industry, where the operating temperature and hydrogen capacity in weight percentage (wt. %) determines the potential of each material. For the maritime industry also a high hydrogen capacity is desirable, preferably close to environmental temperatures.

Sodium borohydride ($NaBH_4$) is one of these materials to store hydrogen. The hydrogen can be generated by hydrolysis, which is an exothermic reaction with water. Acids, catalysts or high temperature can be used to accelerate this process. The material has a relatively large hydrogen fraction, which makes it technically advantageous for storing the energy in a more compact way. Moreover, it is stored under atmospheric conditions, which makes this a safer way to store hydrogen. The companies ‘H2FUEL’ and ‘H2Circular Fuel’ are testing and developing the hydrolysis with ultra-pure water (UPW), filtered deionised water (the most feasibly pure H_2O) [6], and the regeneration of the rest-product (spent-fuel) of the hydrolysis. This technology can be very promising for the maritime industry, although applications and possibilities on-board of vessels are still very unknown.

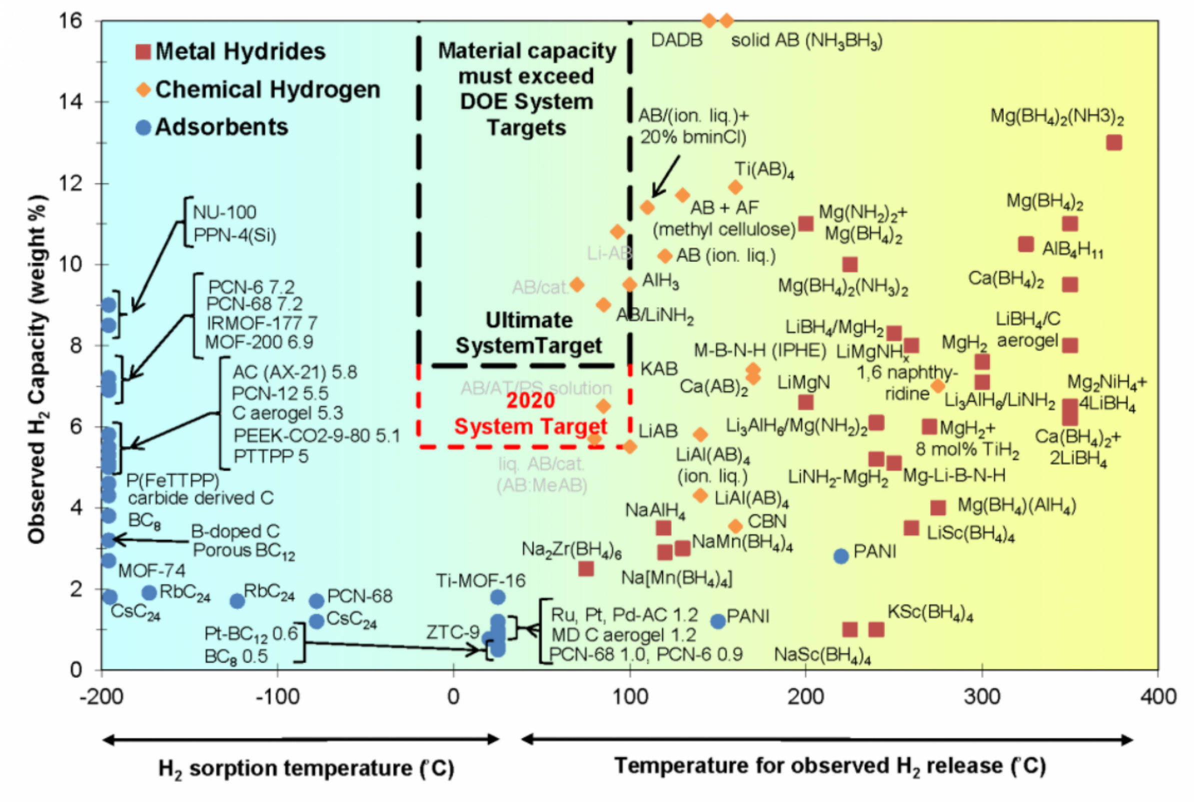

Figure 1.2: Comparison of hydrogen storage materials in hydrogen yield (wt. %) and temperature (°C) [47].

1.1. General background

Material-based storage of hydrogen has been of high interest for a long time, since it has the potential to improve the safety, power density and energy density relative to pressurised or cryogenic hydrogen. Therefore, already many research is performed towards this technology. This section provides a short background and overview of sodium borohydride as energy carrier.

1.1.1. History

The hydrolysis of sodium borohydride was discovered in 1940 by H. I. Schlesinger. In 1953, the first research results towards the hydrolysis of $NaBH_4$ were published [60]. The efficiency and speed of the reaction are compared in this research for different acids and metal salts as catalyst.

The research towards sodium borohydride increased rapidly since 2000, due to the growing interest in cleaner fuels and concerns to the depletion of natural resources [17]. Extended research has been performed on the acceleration of the hydrogen release. A heterogeneous catalyst is commonly used in the reactor, because these are not consumed in the reaction. Other researches were mainly focused towards the fundamentals, scale-up and recycling of the spent-fuel. Especially the companies ‘Millennium Cell’ and ‘Rohm and Haas’ performed many research studies and developed various concepts [57], [76].

In 2007 the U.S. Department of Energy (DOE) reported a no-go for the use of sodium borohydride as energy carrier for the automotive industry[55]. The DOE set targets for 2007 to achieve an amount of system gravimetric capacity of 1.5 *kWh/kg*, a volumetric capacity of 1.2 *kWh/L* and the storage system cost of 6 *$/kWh*. Millennium Cell made a concept using a 30 wt.% $NaBH_4$-solution. This concept almost reached the DOE-targets with a gravimetric capacity of 1.5 *kWh/kg*, a volumetric capacity of 1.22 *kWh/L* and storage system cost of 6.7 *$/kWh*. These values were, however, overly optimistic and required more energy and cost due to the prevention of precipitation of the spent-fuel, according to the DOE. The most important reasons for the DOE to give a no-go recommendation were: the fact that the capacity of the system did not meet the targets of 2010 and the system could not be improved much further to their opinion. Moreover, the solid-state and crystallisation of the spent-fuel in the reactor were causing many problem with regard to the reliability of the system. The U.S. DOE decided to focus on ammonia, another hydrogen storage material, after the results of their report [2, 17].

The amount of research decreased temporarily after the no-go recommendation. Thereafter, the research still continued all over the world because of new possibilities and potentials of this technology. Till now the research towards the different type of catalysts or acids resulted in an improvement of efficiency of the reaction process and an increase in the hydrogen generation rate. The technology has never been commercialised but many tests on application, such as portable devices and cars, has already been performed. One of the best known is the ‘DaimlerChrysler’ car, tested with a catalytic sodium borohydride reactor and fuel cell in collaboration with Millennium Cell [74]. The fuel and spent-fuel in this car were all fully dissolved in water making it easier to handle. The car has never been commercialised because of the low volumetric energy density and the high costs of the system on-board of the car [55].

1.1.2. Working principle of Sodium borohydride as energy carrier

An advantage of sodium borohydride, in comparison with other metal borohydrides, is the high gravimetric hydrogen storage capacity of 10.8 wt% [44]. Sodium borohydride is also one of the most stable metal hydrides to store. The hydrogen can be released by hydrolysis of $NaBH_4$ as is shown in Eq 1.1. This exothermic reaction takes place very slowly under natural conditions, but can be accelerated by adding an acid (increasing the pH value), by catalysis or by increasing the temperature.

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \tag{1.1}$$

The reaction takes place in a reactor where the $NaBH_4$ in a dry or dissolved form is added to the required amount of water and an accelerator. Hydrogen is separated from the spent-fuel in the reactor. The hydrogen can be used in a fuel cell or internal combustion engine and the spent-fuel in the next process where the sodium metaborate $NaBO_2$, or a comparable residue, is regenerated to $NaBH_4$. To stay free from harmful emissions the spent-fuel need to be regenerated by a sustainable source, such as wind or solar energy. Besides hydrogen and the spent-fuel, heat is released in the reactor because the reaction shown in Equation 1.1 is exothermic. This heat can be used to heat up the reactor to improve the speed of the reaction. The rest of the heat can be used for other purposes, such as for the heating systems on-board of the vessel.

1.1.3. Possibilities for the maritime industry

The use of sodium borohydride as an energy carrier has many potential advantages, such as an (harmful) emissions-free fuel, a safe fuel, and a recyclable fuel. These advantages can be applied for many application, such as on cars, planes and energy storage plants. The maritime industry offers, however, some additional advantages making it an even more interesting technology. Most important is the fact that vessels are surrounded with water, which can be used for the hydrolysis of sodium borohydride. Another advantage in comparison with the automotive industry is the availability and transportation of sodium borohydride on land, because less fuel and regeneration points are needed, especially when one specific sailing profile is used, like on a liner trade.

1.2. Goal of the research

In this master thesis the opportunities of the use of sodium borohydride as an energy carrier on-board of vessels will be studied. The goal is to give an insight and advise on the implementation of this technology in the maritime industry. The focus of the project will be on some of the important elements determining the feasibility of the system. These elements include:

- The consequences in the technical design of a drive train
- The gravimetric and volumetric power density
- The gravimetric and volumetric energy density
- The efficiency
- The dynamic behaviour between the subsystems, based on one specific application on the Clipper Stad Amsterdam

The project should give a clear overview of the applications and possibilities for the future use of this type of systems on-board of vessels.

1.3. Problem definition

As described earlier, there are some challenges using a sustainable fuel such as hydrogen. The use of a storage material like sodium borohydride has high potential to offer a more compact solution, but it is still very difficult to meet the targets of the DOE shown in Table 1.1 [2] and entirely in Appendix A. Dealing with the volumetric and gravimetric energy density is an import challenge for this technology. Moreover, practical issues such as the crystallisation and solubility of the spent-fuel needs attention.

Implementation of the system in the maritime industry has a high potential to reduce harmful emissions. The system can be implemented using different components such as fuel cells, combustion engines, or by using different types of sodium borohydride solutions. There is a need to have a clear overview of the possibilities and feasibility of the system on-board of vessels.

Table 1.1: Department of Energy: Technical system targets for hydrogen storage [2]

STORAGE PARAMETER	UNITS	2020	2025	ULTIMATE
System Gravimetric Capacity				
Usable, specific-energy from H2	kWh/kg	1.5	1.8	2.2
(net useful energy/max system mass)	(kg H2/kg system)	(0.045)	(0.055)	(0.065)
System Volumetric Capacity				
Usable energy density from H2	kWh/L	1.0	1.3	1.7
(net useful energy/max system volume)	(kg H2/L system)	(0.030)	(0.040)	(0.050)

1.4. Research questions

Using the problem definition the following research question is defined:

How does a technical design of a power train using sodium borohydride as hydrogen storage material on-board of vessels perform in terms of power and energy density and in a transient load?

To find an answer to this question the problem is divided in the following sub questions:

1. *What are the opportunities in a technical design using sodium borohydride on-board of vessels as an energy carrier?*
2. *How do the possible components and configurations perform in terms of overall system efficiency on-board of a vessel?*
3. *How do the possible components and configurations perform in terms of gravimetric and volumetric power and energy density on-board of a vessel?*
4. *How does the system behave in a transient load on one specific configuration of the 'Clipper Stad Amsterdam'?*

The questions are all focused to give a clear overview and insight in the opportunities and feasibility of this technology. The answers to these questions will be a useful starting point when the technology is implemented in the design of a vessel.

1.5. Scope of the research

A scope has to be defined to make this research feasible in the time of a master thesis at the TU Delft. The most important part of the scope can be concluded from the research question and the sub-questions. The performance parameters covered in this research are: the efficiency, the density, the safety and the dynamic behaviour of a sodium borohydride system on-board of a vessel. Other important parameters such as environmental impact and the financial feasibility will not, or just shortly be described in the report. The system boundaries are set on the process on-board of the vessel and, therefore, the regeneration of the spent-fuel on land is not taken into account.

The scope is further defined by the scenarios taken into account in this research:

- Fuel type ($NaBH_4$-concentration): Dry, concentrated and saturated.
- H_2O Addition: separate tank, from the fuel cell, produced on-board (reverse osmosis) or a combination of this option.
- Spent-fuel: filtered or liquid.
- Accelerators: catalyst, acid addition and high temperature.
- Spent-fuel tank: separate tank, volume-exchange tank or a ballast integrated tank.
- Hydrogen conversion: Low Temperature Proton-Exchange Membrane Fuel Cell (LT-PEMFC), High Temperature Proton-Exchange Membrane Fuel Cell (HT-PEMFC), Solid Oxide Fuel Sell (SOFC).

Multiple fuels are considered in this research. All water needed in the process can be added on forehand. This results in a saturated basic solution where all sodium borohydride is dissolved in the water. This is the most simple and well known option to implement. Research has shown that this system has difficulties to meet the targets in volumetric energy density [55]. A more compact fuel can be obtained by using a higher concentration or even pure sodium borohydride (dry fuel). In this case water has to be added in a later stadium of the process, before the reactor. Water can be stored on-board in a separate tank, or it has to be produced on-board by making use of reverse osmosis and/or by recycling the water from the fuel cell.

It is preferable that the spent-fuel is as concentrated as possible, without blocking the reactor or influencing the efficiency. This will determine the stoichiometric ratio and the viscosity of the spent-fuel. First of all, a separate tank will be used for the calculations. Thereafter, a volume-exchange tank, which is still in concept, is taken into account. In this tank the fuel and spent-fuel are stored in one tank in separated compartments. The volume of each compartment can change whereby no extra volume is needed. This concept-tank is not proven on big scales, such as on a drive train of a vessel, but has a high potential to improve the performance on volumetric system density.

Both the PEMFC and the SOFC are considered for the hydrogen conversion after the reactor, because they offer different advantages, highly dependent on the type of application. It will, therefore, be useful to provide a comparison of the consequences in the design of both technologies. Other options are not or shortly discussed in this thesis. The internal combustion engine is not included, because this will be covered in other researches. The Direct Borohydride Fuel Cell (DBFC) is an option where a sodium borohydride solution can directly be used in a fuel cell. The DBFC would be very optimistic to take into account [71] and will, therefore, be excluded in this research.

To study the dynamic behaviour of a sodium borohydride system on-board of a vessel, a model is made of one specific application. The dynamic behaviour will include the performance in a fluctuating load on a typical trip of the Clipper 'the Stad Amsterdam' (CSA). Moreover, the fuel weights and volumes will be compared to the results calculated in the first part of the research.

1.6. Research content

The research questions describe the assignment very shortly and indicate a possible solution to the problem definition. In the first sub-question the technical design is going to be studied and all possibilities, using this system on multiple vessel configuration, will be listed and described to give a clear overview of the opportunities.

The possibilities will be tested on its performances in the sub-questions 2 and 3. The efficiency, gravimetric and volumetric power and energy density are important performance parameters concerning the feasibility of this technology. These results can also be a useful starting point to determine the costs and environmental impact of the technology. The parameters will be defined for different scenarios mentioned in the scope of the research. First, the parameters will be determined for each component separately and, thereafter, the components are added together to provide a final result for the whole system. The parameters for the fuel handling system will be estimated with a bottom-up approach, where each volume and weight will be determined separately. A top-down approach will be used for the rest of the drive train, using the data of review researches and comparable systems. Ragone plots for each scenario will be provided and compared to other fuel systems in the maritime industry. In the end of this part the safety issues of the system are determined and existing or comparable regulations are analysed.

The dynamic behaviour is analysed in the second part of the research. A model is build to provide an accurate answer to the last sub-question. One specific application on-board of the ‘Stad Amsterdam’ is chosen, because it is impossible to model all opportunities within this research, .

1.6.1. Model of a sodium borohydride system on-board of the ‘Stad Amsterdam’

A sodium borohydride system on-board of a vessel is a complex system where multiple system components interact with each other, especially when residual fuels, such as the water from the fuel cells, are recirculated in the system. The system becomes hard to predict when the input parameters are changing over time, such as in a transient load. In this case a model can help to get a better understanding of the behaviour of the system. Besides the complexity of the system, this technology is not fully developed yet on this scale. Therefore, a model is used for the verification of the results and implementation of a system on-board of vessels [70].

The model represents a concept-configuration, which is evolved from the feasibility study on the Clipper the Stad Amsterdam. The CSA is one of the best known sailing vessels of the Netherlands. This 56 m long vessel is used as a luxury cruise vessel sailing all over the world. The vessel is mainly propelled by the wind, but obviously, multiple engine are installed on-board. The prime mover is a 750 kW diesel engine and two generators of 156 kW deliver their power to the hotel- and auxiliary load.

To make the CSA even more environmental friendly (because it is already a sailing vessel), the shipping company decided to investigate the implementation of a sodium borohydride system. The results of this thesis are used for a feasibility study together with the company Damen Bergum. This study was focussed on: the volumes, weights, lay-out and technical consequences. Furthermore, the results of the feasibility study on the CSA are used to build the model and study the dynamic performance of the concept.

1.7. Structure of the report

This report is divided in three parts. In the first part (Chapters 2 to 6), an answer on the first three sub questions will be given mainly based on a literature study. The chapters are divided in the different components of the drive train of a vessel. The second chapter includes the description and calculations on the fuel handling system. Thereafter, different types of fuel cells are analysed on its performances and in chapter 4 the rest of the components after the prime movers are included. Hereafter, the results of the sub-systems will be combined in the possible configurations dependent on the scenario's. Now a total system overview can be given on the densities and efficiencies when the technology is implemented on a vessel. Finally, a safety study is done to conclude or predict some additional technical consequences.

The next part (Chapter 7 and 8) deals with the last sub-question and will describe the model that has been made. First the model and simulation is described in chapter 7. Especially the CSA is studied to define a system boundary and the input parameters. Chapter 8 describes the simulation input and Chapter 9 provides the results and corresponding analyses. In the last part (Chapter 10) the conclusions and recommendations are presented.

I

Technical design, efficiencies and densities

2

Fuel handling

The fuel handling system of the drive train is the most innovative part of the system, because it is hardly implemented on commercial scale and even less unknown for the maritime industry. A bottom-up approach is used to provide a sufficient estimation of the energy and power density of the sub-system. Therefore, each component of this system is analysed separately. The sum of the components result in a total energy and power density of the fuel handling system. The following components are included within de boundary of this sub-system: the fuels, the fuel tanks, the fuel processing and the reactor. Components of these sub-systems and the structure of this chapter is presented in Figure 2.1.

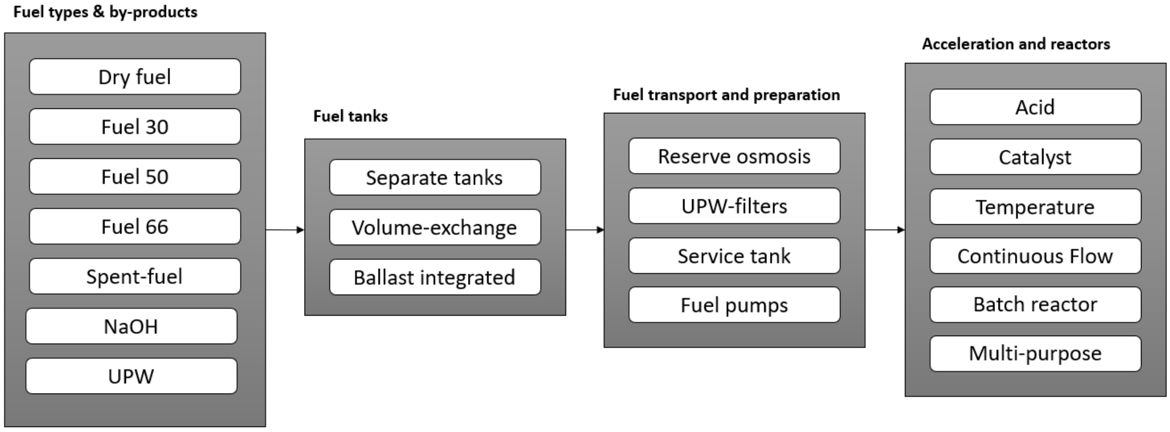

Figure 2.1: Overview of the components and possibilities in the fuel handling system

2.1. System overview

An overview of the flows in this subsystem is shown in Figure 2.2. Here each subcomponent of the fuel handling system is shown. Not all components are representative for each configuration. The desalination of seawater, for example, is not relevant when all water is already stored on-board. Moreover, the choice of the reactor will influence the amount of components needed for this subsystem. The gravimetric and volumetric power or energy density can be determined for each option in this overview. The range of this system-density will vary between the maximum and minimum values of each component.

The energy density will be defined as "the amount of electrical energy available per unit of either mass or volume"[69]. In the case of this subsystem this will be the energy potential in the hydrogen released by the reactor, because this is the output of the sub-system. The size and weight of the components/subsystems necessary to produce the required amount of energy are taken into account in the calculation of the energy density. For this sub-system the fuels and fuel-tanks.

The power density will be defined as the amount of power available per unit of either mass or volume [69]. An important difference is that these systems consume or produce energy and are, therefore, dependent on the amount of energy over time. The components considered for the power density will scale based on the power installed on-board of the vessel. For this sub-system, this includes: the reactor, the filters, the service tanks and the pumps.

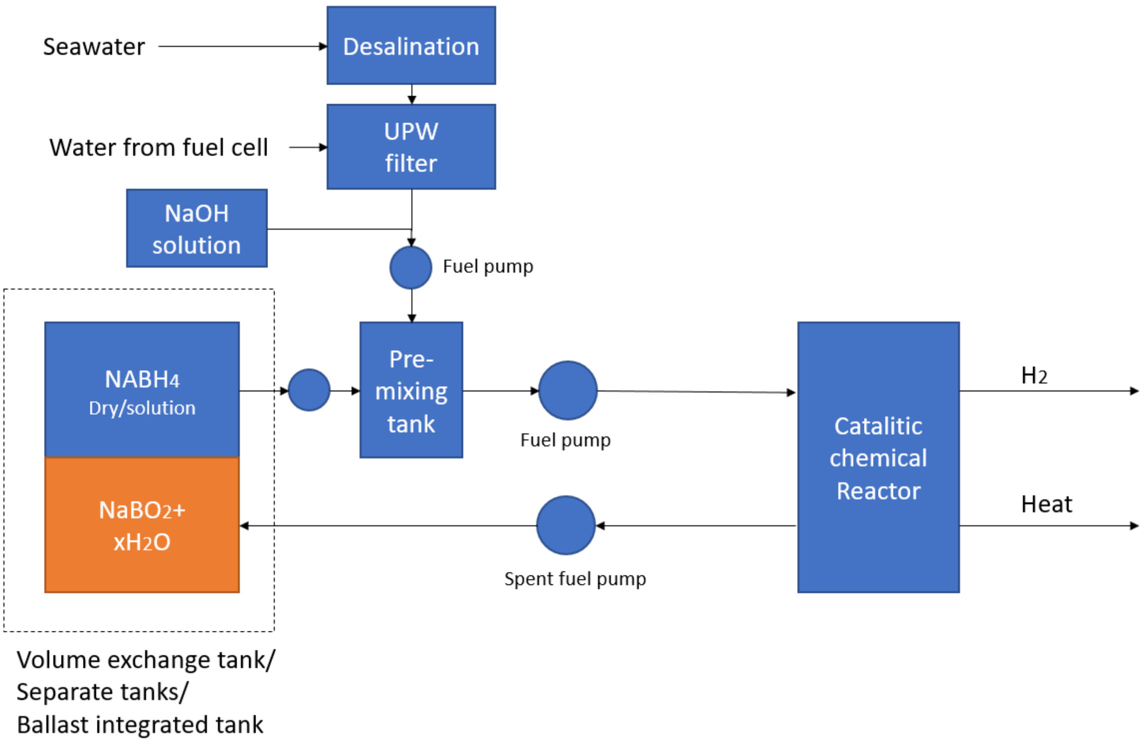

Figure 2.2: Overview of the fuel handling subsystem

2.2. Fuel types and products

In the system many fuel-types can be used. A design choice can be made between compact fuels, such as a dry fuel and fully dissolved fuels, such as a sodium borohydride solution in water, which is easier for transportation on-board of the vessel. All fuels have their own advantages and disadvantages. Energy densities and technical consequences will be discussed for each fuel type. The results are used to estimate the fuel weights and volumes for some concept applications presented in Appendix D.

2.2.1. Sodium borohydride

The enthalpy differences in a combustion of a chemical substances is normally used to calculate its higher heating value (HHV) or lower heating value (LHV). The enthalpy can be interpreted as the "energy to create a system plus the work needed to make room for it"[48], which is also shown in Equation 2.1.

$$H = U + pV \tag{2.1}$$

Where U is the internal energy in joule, p the pressure in Pascal and V the volume in m^3. The energy content in sodium borohydride can now be calculated using the enthalpy differences, shown in Table 2.1. Equation 2.2 and 2.3 shows the reaction of the combustion of sodium borohydride to calculate the potential energy.

$$NaBH_4 + O_2 \rightarrow NaBO_2 + 2H_2O \tag{2.2}$$

$$(-188.6+0)-(-977.0+2\cdot -285.8) = -1360.0[KJ/mol] \tag{2.3}$$

Dividing this result by the Molar Mass of 37.832 g/mol [11] results in a HHV of 35.95 MJ/kg. It has to be noticed that these calculations give the ideal value for each fuel. Parameters like grain size and impurities are not taken into account, so in the calculations a theoretical value is used, such as it's done for MGO and other fuels. An overview of all properties of sodium borohydride together is provided in Appendix B.

Table 2.1: Enthalpy of combustion reaction

	$\Delta H[kJ/mol]$	$\Delta G[kJ/mol]$
$NaBH_4$	-188.6	-123.9
H_2O	-285.8 (l)	-237.1
H_2O	-241.8 (g)	-228.6
O_2	0.0	
$NaBO_2$	-977.0	-920.7
H_2	0.0	

The same energy potential can also be calculated by adding the potential energy out of hydrogen to the heat released by the hydrolysis of sodium borohydride. 4,7 kg $NaBH_4$ is needed to generate 1 kg of H_2. The energy content of the hydrogen, using 1 kg of $NaBH_4$, can now be calculated using the HHV of hydrogen (141.7 MJ/kg), as can be seen in Equation 2.4.

$$\frac{141.7}{4.7} = 30.15[MJ/kg] \tag{2.4}$$

The heat released from the exothermic reaction shown in Equation 2.5 is calculated in Equation 2.6 using the enthalpy differences.

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \tag{2.5}$$

$$(-188.6 + 2\cdot -285.6) - (-977.0 + 0.0) = -216.8[kJ/mol] \tag{2.6}$$

216.8 kJ heat is released for each mol of sodium borohydride in the reaction. Dividing this by the molar mass, results in 5.73 MJ for one kilogram of sodium borohydride. Adding this to the energy content in the hydrogen out of 1 kg sodium borohydride, results in a HHV of sodium borohydride of 35.88 MJ/kg, which is close to the previous calculation.

Both methods to calculate the energy content will be used in this research. For chemists it is most of the time more interesting to know what the characteristics of the reaction are and they will, therefore, translate to energies at a later stadium of the process. For a system-integrator it is most of the time more interesting to know the energy content in a earlier point of the process. Therefore, two different reactor efficiencies are known. The hydrogen generation efficiency η_{H_2} is the amount of hydrogen which gets out of the reactor over the amount of hydrogen in sodium borohydride and the stoichiometric water part of the reaction (2 mol H_2O against 1 mol $NaBH_4$). Typical efficiencies above 90 % can be found is researches [28]. In the reactor efficiency $\eta_{reactor}$ the amount of energy into the reactor is devided by the amount of energy out of the reactor. This can also be seen as the energy content in the sodium borohydride and the energy content in the hydrogen which flows out of the reactor. In this case the heat from the reaction is already taken into account. Here, typical efficiencies around 80% can be expected. Both efficiencies are shown in Equation 2.7 and 2.8.

$$\eta_{H_2} = \frac{n_{H_2,out}}{n_{H_2,in}} \tag{2.7}$$

$$\eta_{reactor} = \frac{E_{H_2,out}}{E_{NaBH_4,in}} \tag{2.8}$$

Where n is the number of mol for both the reactants and the hydrogen, and E the chemical energy in Joule in the hydrogen and sodium borohydride. In this chapter the hydrogen generation efficiency is used.

2.2.2. Fuel 30

In practice more water is needed for the process, as is shown in Equation 2.9.

$$NaBH_4 + (2+x)H_2O \rightarrow NaBO_2 + 4H_2 + xH_2O \tag{2.9}$$

where x represents the extra water needed in the reactor in mol. The water can be stored separately, produced on-board or recycled from the fuel cell. The water can also be added to the dry sodium borohydride on forehand. In this case the fuel need to be made stable by adding a base. Most used base for this solution is $NaOH$, which will be described further in this chapter. Experiments show that the extra water added to the process

Table 2.2: Weights in the reaction of the hydrolysis of sodium borohydride

$NaBH_4$	+	$(2+x)H_2O$	$\rightarrow$	$NaBO_2$	+	$4H_2$	+	xH_2O	
						1			kg
124		(248+372)	→	124		992		372	mol
4.7		(4.5+6.7)	→	8.2		1		6.7	kg

is around 3 mol for 1 mol sodium borohydride [44]. This to prevent crystallisation in the reactor. This leads to a total of 5 mol water needed for this process. To generate 1 kg of hydrogen 4.7 kg sodium borohydride, 4.5 kg water and 6.7 kg additional water is needed. To stabilise this solution a typical 5 wt.% of $NaOH$ is added to the solution. Adding this together results in 16.2 kg Fuel 30 for 1 kg of hydrogen. An overview of the weight in the reaction is shown in Table 2.2, This results in a weight percentage of approximately 30 wt.% and, therefore, this is called Fuel 30. The energy density also decreases with 70% because the water is stored on-board. Comparing with other fuels the HHV or chemical energy will become 10.4 MJ/kg. The volumetric density becomes 14.6 MJ/l, when using a density of 1.4 g/ml.

The density of sodium borohydride is 1.07 g/ml at 25 °C [11]. The volume can not be calculated by adding the volume of the water with the volume of the dry powder when they are mixed together, because the sodium borohydride absorbs the water and crystals like $NaBH_4 \cdot 2H_2O$ are formed. The solubility as calculated by 'Rohm and Haas' is shown in figure 2.3 [57]. At room temperature a $NaBH_4$-solution is limited to 35 wt.%. Therefore fuel 30 is fully dissolved in the water. The volume of the powder need to be added to this limit when more sodium borohydride is added. The density of fuel 30 is estimated experimentally resulted in a value of 1.4 g/ml [57].

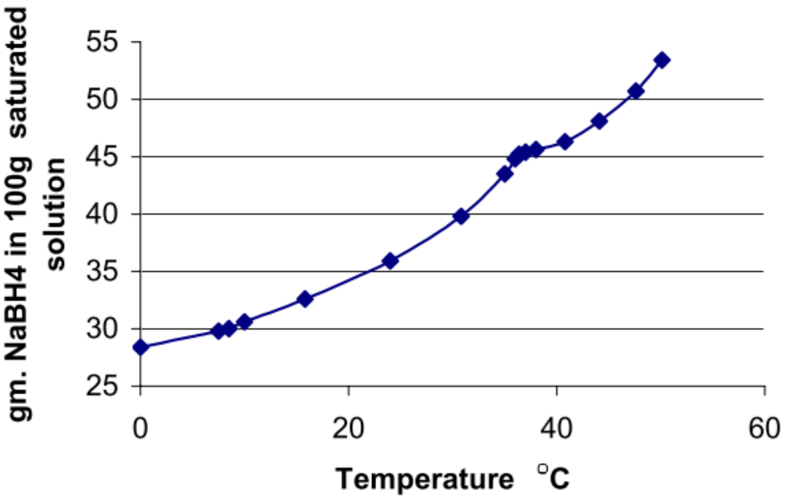

Figure 2.3: The solubility of sodium borohydride in 100 gram saturated solution at different temperatures [57]

2.2.3. Fuel 50

Fuel 50 is based on the same principle as Fuel 30. The weight percentage of Fuel 50 is around 50 wt.%. This percentage is based on the amount of water, which has to be added to the process in combination with an acid accelerator. HCL is always stored in a solution. The amount of water in the HCL-solution together with the water in Fuel 50 is the same as the total water needed for this process (5 mol for one mol $NaBH_4$). More $NaOH$ has to be added to this fuel (typically 7.5 wt.%) because the solution is more concentrated, as is also explained later in this chapter.

As is illustrated in Figure 2.3 [57] Fuel 50 is not fully dissolved at room temperature. At a higher temperature, such as in the mix-chamber, the $NaBH_4$ and $NaOH$ is dissolved in the water. Therefore, no blockage will occur during the injection of the solution, when the temperature is high enough. In the tank-design it has to be taken into account that solid particles will form and, therefore, circulation in the tanks will be needed.

The density for Fuel 50 can be calculated using the same method, resulting in 18.0 MJ/kg. The density lies between the density of Fuel 30 and the dry powder, since there are some solid particles in the fuel. Just a small percentage of this fuel consists of particles. Therefore, a density of 1.3 g/ml is assumed for further calculations, resulting in a volumetric energy density of 23.4 MJ/l.

2.2.4. Fuel 66

Fuel 66, or the slurry fuel, has a weight percentage of 66 wt%. This weight percentage is based on the theoretical amount of water which can be recycled from the fuel cell. The water from the fuel cell and the water in Fuel 66 together is enough for the process to continue.

From Figure 2.3 it can be seen that 35 wt% of the solution is $NaBH_4$ at ambient conditions. The total weight of the water and solved $NaBH_4$ is shown in Equation 2.10.

$$\frac{0.34}{1-0.35} = 0.523[kg] \tag{2.10}$$

Where 0.34 is the percentage of water in the fuel and 0.35 the percentage which can be dissolved at room temperature. This results in 0.523 kg fully solved solution containing 0.183 kg $NaBH_4$. The rest of the fuel (0.477 kg) is pure $NaBH_4$. By combining the densities of the dissolved and solid form the weight of 1 l 66% fuel is determined, like shown in Equation 2.11.

$$\frac{1}{\frac{0.523}{1.4}+\frac{0.477}{1.07}} = 1.22[g/ml] \tag{2.11}$$

This results in a density of the 66 wt.% fuel of 1.22 kg/L. The energy density can now be determined, resulting in a gravimetric energy density of 23.7 MJ/kg) and a volumetric energy density of 28.9 MJ/L.

2.2.5. Fuel comparison

A comparison of the energy content in other fuels is made, as is illustrated in Figure 2.4 [21]. It is important to notice that this figure only takes into account the density of the fuel and not the system needed to operate with this fuel. The energy density of liquid hydrogen becomes relatively low when the weight of the system is accounted, due to heavy tanks that are required to store the fuel at -253 °C. Still the figure provides a useful overview of the potential of the fuels. The figure also demonstrates the challenge sustainable fuels have to overcome to compete with fossil fuels, because the high density of fuels like MGO and HFO. The energy density of sodium borohydride is shown in orange for: the dry fuel, fuel 66, fuel 50 and fuel 30. The dry powder or grains of sodium borohydride have a density that is getting close to the density of diesel, HFO and MGO. Unlike diesel, water has to be added to the sodium borohydride for the hydrolysis resulting in a lower gravimetric and volumetric energy density unless the water from other resources is used. For this reason, recirculation of the water from the fuel cell and from the environment will be taken into account later in this chapter. The 66 wt.% solution of sodium borohydride and water is still pumpable, according to H2 Circular Fuel [64]. In this form the density comes close to methanol and ethanol. The energy content in fuel 66 becomes lower in gravimetric energy density, because the weight of the water is included. The volumetric density decreases not as fast, because of the absorption of the water in sodium borohydride.

Another comparison can be made by comparing different types of hydrogen storage materials, such in done in Figure 1.2 [47]. This graph shows the variety of materials, which can be used to store hydrogen. The most important and potential materials according to the DOE are shown within the system targets of 2020 and the ultimate target. As can be seen in the figure, ammonia borate has a high potential due to its high hydrogen yield and the acceptable operating temperature. Sodium borohydride is not shown in this graph, but effective capacities have been reported between 6.7 wt% for a liquid fuel and 9 wt% for the dry fuel, around room temperature. Here the system as a whole is not taken into account [17]. In section 2.7.1 the size and weight of the systems in different scenarios will be calculated.

2.2.6. Spent-fuel

As mentioned before in Section 1.1.1, the handling of the spent-fuel is a challenge when a compact system is desirable. These problems have to do with the low solubility of the spent-fuel $NaBO_2$. At first, it becomes challenging to transport this material to and out of the tank. Secondly, many problems have been reported on the crystallisation in the reactor; it makes the reaction less efficient or even impossible. An overview of the phases of the spent-fuel and the type of crystals at different fractions is demonstrated in Figure 2.5. For example, when 1/3 of the spent-fuel is $NaBO_2$ in molar fraction, typically crystals such as $NaBO_2 \cdot 2H_2O$ and $NaBO_2 \cdot 4H_2O$ are formed at room temperature. Arizona state university found that many other boron oxide

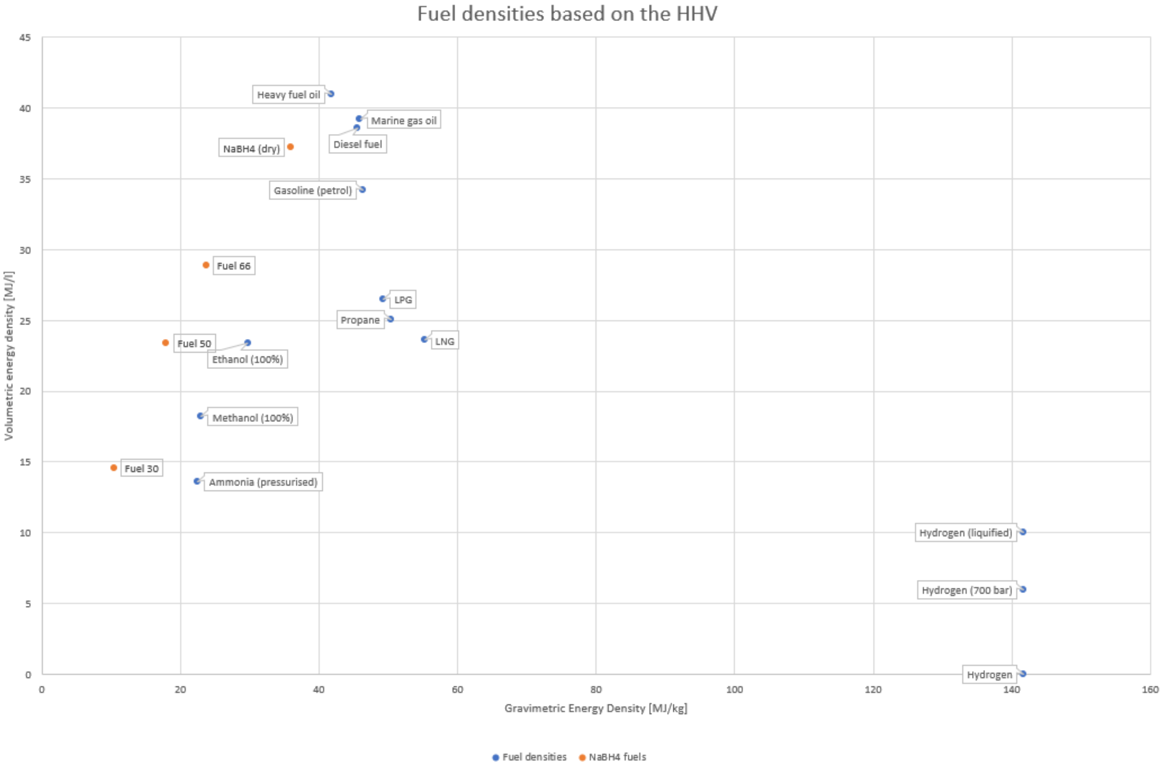

Figure 2.4: Comparison of the higher heating values of fossil and renewable fuels in the maritime sector [21].

can be formed, such as $Na_2B_4O_7$ and $Na_2B_4O_5(OH)_4 \cdot 3H_2O$ [27]. The type of products in the spent-fuel can vary and are dependent on the type of application and the operating temperature. To study the behaviour of the spent-fuel a chemical analysis is needed for each application. The weight of the spent-fuel will not change significantly, because the same amount of hydrogen is released from the fuels. The weight of the spent-fuel can, therefore, be determined by adding the weights of the reactants minus the hydrogen released from the mix-chamber. The spent-fuel volume density is more challenging and is often determined experimentally.

There are solutions to make the handling of the spent-fuel easier and to prevent crystallisation. As mentioned before and illustrated in Figure 2.5 and 2.6, higher temperatures are improving the solubility of the spent-fuel. Moreover, more water addition in the process is an effective method to overcome this challenge. This has, however, the disadvantage that the energy density of the system decreases, when this extra water is stored on-board.

As can be concluded from Figure 2.6, 100 grams of water is needed to completely dissolve 1 mole of $NaBO_2$ together with the water needed for the hydrogen generation, in case the temperature lies between 80 °C and 100 °C and no stabiliser is added. Dividing this by the molecular weight of H_2O (M =18.015 g/mol) results in 5.55 mol water. This is 2.75 times the stoichiometric ratio. In practice a lower value can be reached, because a relatively small amount of crystals would not immediately block the reactor or the pipelines. ‘H2Fuel systems’ uses a ratio of 2.5, determined experimentally.

2.2.7. Sodium hydroxide

Sodium hydroxide is often used in the fuel to stabilize a sodium borohydride solution. The solution becomes more basic and, therefore, more stable at higher concentrations of sodium hydroxide. The relation between acidity and half-life of the solution is shown in Table 2.3 [27]. A typical percentage to use is in the range of 0 - 10 wt% sodium hydroxide, dependent on the required half-life and the concentration of the solution. In this thesis the values of H2Circular fuel will be used of 5 wt. % for Fuel 30, 7.5 wt.% for Fuel 50 and 10 wt.% for Fuel 66. These ratios result in a pH-value between 13 and 14 and a half-life between 42.6 and 426.3 days, sufficient for the use on-board of vessel [64]. The density of sodium hydroxide is 1110 kg/m^3. Other characteristics can be found in Appendix B.

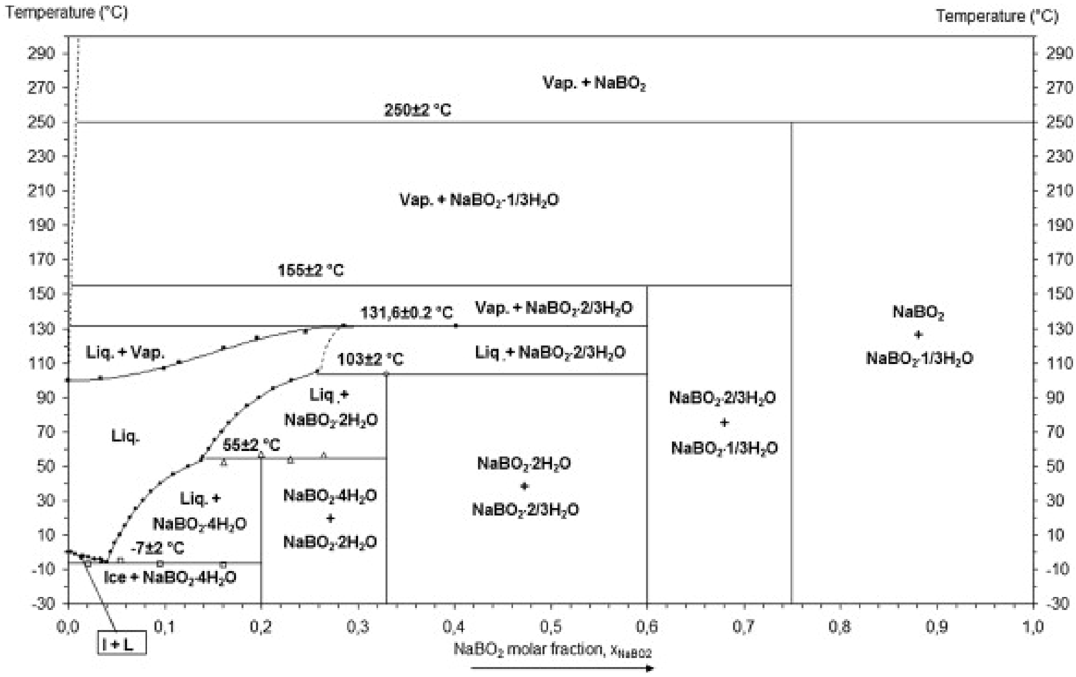

Figure 2.5: Phase diagram of the system $NaBO_2 - H_2O$[4]

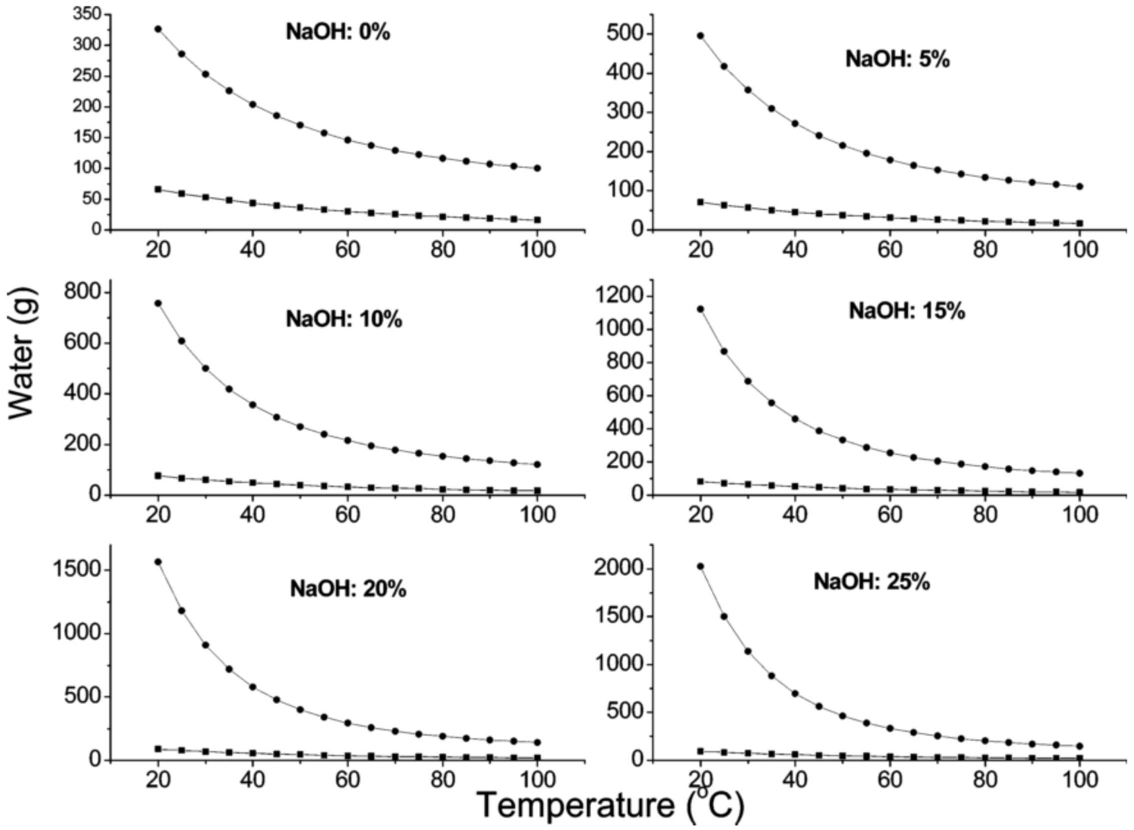

Figure 2.6: Quantity of water needed to dissolve 1 mole of $NaBO_2$ and to react with 1 mole of $NaBH_4$ (•) compared with the quantity of water contained in saturated $NaBH_4$ solution (■) [61]

2.2.8. Ultra pure water

A way to improve the hydrogen generation efficiency is to make sure the fuels are as pure as possible. Therefore, in the past, most of the time de-ionised water has been used for the reaction with sodium borohydride.

Table 2.3: Stability of a sodium borohydride solution [27]

pH	NaBH4 Half-life	
4.0	0.0037	s
5.0	0.037	s
5.5	0.12	s
6.0	0.37	s
7.0	3.7	s
8.0	36.8	s
9.0	6.1	min
10.0	61.4	min
11.0	10.2	hours
12.0	4.3	days
13.0	42.6	days
14.0	426.3	days

An even more pure form of H_2O can be used in the form of ultra pure water (UPW). Ultra pure water is well known in the semiconductor industry. The main difference between UPW and de-ionised water is that organic particles are removed resulting in a more pure reaction and, therefore, a higher hydrogen generation efficiency in the reactor. H2Fuel-systems b.v. patented this method and claims to reach a hydrogen generation efficiency of 98% [64, 73]. Ultra pure water can be stored on-board of the vessel, however, in the situation where water is produced on-board or recycled from the fuel cell, the water need to be filtered on-board, as discussed later in section 2.4.2. Ultra pure water can be classified in different types, with various requirements of impurities in the water. Inventor G. W. Lugtigheid defines the ultra pure water used for the hydrolysis by: "having an electrical conductivity less than 1 pS/cm and an ASTM type E-1 rating or higher"[73]. The ASTM is the American Society for Testing and Materials. The density in weight and volume is getting very close to that of H_2O (18.015 g/mol and 997 kg/m^3), because of the high purity of the water and will, therefore, be used in the calculations. Further characteristics of ultra pure water can be found in Appendix B.

2.3. Fuel tanks

Storage of the sodium borohydride can be done in several ways. The most compact way is the dry form, where almost pure $NaBH_4$ can be stored in powder or grains. The energy density is the highest in this form. Fuel handling is still a challenge, because the transportation of a solid material in powder form is less known within the maritime sector. In the case Fuel 30, 50 or 66 the transport from the tanks becomes easier. Both methods will be taking into account for the fuel tanks. First, separate fuel tanks are analysed and, thereafter, the volume-exchange principle will be explained. Both technical consequences and energy densities will be discussed.

2.3.1. Separate fuel tanks

Fuels used in these systems are most of the time stored in composite tanks. For example, typical composite 1000 litre Intermediate Bulk Containers (IBC) are used on a pallet. To make an estimation of the size and weight of a storage tank like this, multiple types of composite storage tanks are shown in Appendix C . By calculating the average weight and volume of the storage tank, the density becomes 63 $kg/1000l$ of fuel and 1.4 $m^3/1000l$ in box-volume. To store 1000 liter of fuel a tank of 1.4 m^3 and 63 kg is needed. Translating this to percentages results in a volume-increase of 39% and weight-increase of 6%. The weight of the tank is expressed in the amount of fuel stored in the tank in liter. When, for example, 1000 liter fuel is needed for the storage of a ‘slurry’ fuel the box volume of the tank becomes 1.4 m^3 with a tank weight around 63 kg.

A portable chemical container can be considered in case higher storage volumes are required. With the high or low pH-values a rubber-lined International Organisation of Standardization (ISO-) tank container should be able to store the fuels. These 20’-containers have a dimension of 6060 x 2440 x 2590 mm and a weight of 3650 kg. The capacity of this container is up to 21000 liter. In the design of the first liquid natural gas (LNG) applications these containers are also used. In these cylindrical tanks the ratio between box volume and cylinder volume determines the extra space needed for the tank. In this case 38,3 m^3 is needed to store 21,0 m^3 fuel. This is equal to a 1.87 m^3 fuel-tank of 173 kg for each m^3 of fuel stored. This results in a weight addition of 73% per unit inner volume and 87% extra volume needed per volumetric unit of fuel.

2.3.2. Volume-exchange tank

The energy density of the system will decrease rapidly when the spent-fuel is stored on-board. This spent-fuel need to be stored on the vessel with some extra water added to make the product pumpable and to prevent blockage in the reactor or in the tank system. This means that during the trip the vessel becomes heavier, and that extra storage volume is needed. This affects the gravimetric and volumetric density significantly and it is, therefore, important to investigate technical solutions for this increase in volume and weight. One of these solutions is the use of a volume-exchange tank. In this tank two or more fuels are stored, where the inner tanks change in volume. During the trip the spent-fuel tank becomes bigger and the fuel tank smaller.

Such a tank system is researched by Kim Taegyu, who analysed a system as is illustrated in Figure 2.7 [34]. This application has a maximum power output of 100 W from the PEMFC and has a storage capacity of 107.8 $W \cdot h$ with 200 gr of 15 $wt\%$ $NaBH_4$ and a Co-B catalyst. A rubber bag is designed in the tank to store the spent-fuel, like shown in the figure. As is concluded from this research the volume-exchange tank in this configuration improved the volumetric density, and on top of that the gravimetric density. After all, two tanks are heavier than one volume-exchange tank. Other advantages are that the effect of sloshing and the change in center of gravity were minimised [34]. These advantages will also be applicable when a scale-up system on-board of a vessel is implemented.

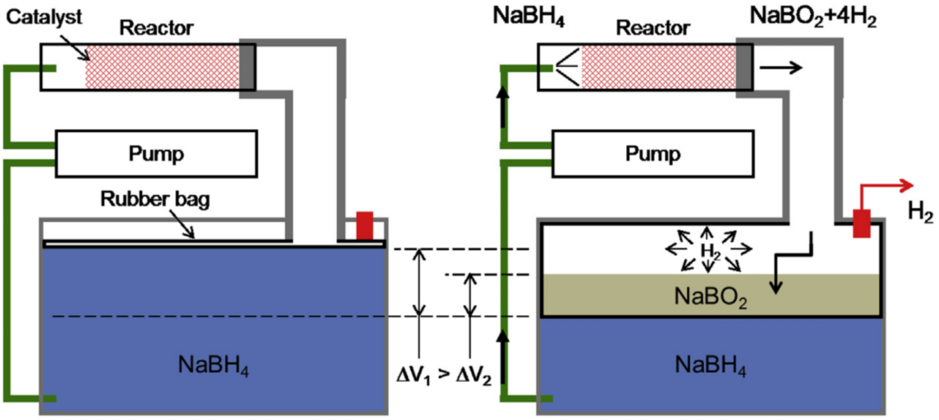

Figure 2.7: Operation concept of a volume-exchange fuel tank for a small UAV (unmanned aerial vehicles) [34]

Another example of a volume-exchange tank is the one suggested by H2Fuel-systems, shown in Figure 2.8 [64]. In their concept 3 compartments can change in volume due to flexible inner tanks. This design can be applicable on a system where acid as an activator is used, stored in the third compartment. Two situations are shown in this figure. One where the spent-fuel volume is maximised and the vehicle needs to re-fuel, and one when no fuel is consumed yet [64]. In maritime application this tank will improve the volumetric and gravimetric energy density when an acid accelerator is used. A disadvantage of this system is the safety hazard of storing an acid and a sodium borohydride solution in one tank.

A new concept design is herein proposed, which overcomes the safety hazard of the previously mentioned tank. This concept is depicted in 2.9. In this concept a dry fuel- spent-fuel volume-exchange tank is suggested. The shaded and technical view shows a bag in the top of the tank where the spent-fuel is stored in a solid or liquid condition. Under this bag a moveable membrane lifts the weight of the spent-fuel. The rest of the tank is the space for the dry fuel in the form of a funnel to control the amount of fuel added to the water flow system under the storage tank. In this concept, gravity is used to handle the dry fuel. Another option would be to handle the dry fuel pneumatically.

In the scenario where a volume-exchange tank is used the volumetric and gravimetric density of the system will change. The size and weight of the tank will be dependent on the most voluminous fuel stored in the tank. At room temperature, the density of dry $NaBH_4$ is 1.07 g/ml. For 1 gram, 0.97 ml inner storage volume is needed. One gram of $NaBH_4$ (0.0264 mol) and, from the hydrolysis reaction, 1.74 grams of $NaBO_2$ (0.0246 mol) is needed. $NaBO_2$ has a density of 2.46 g/ml, so for each gram of $NaBH_4$ a volume of 0.71 ml is needed for the spent-fuel. This means the spent-fuel becomes heavier and less voluminous in dry conditions.

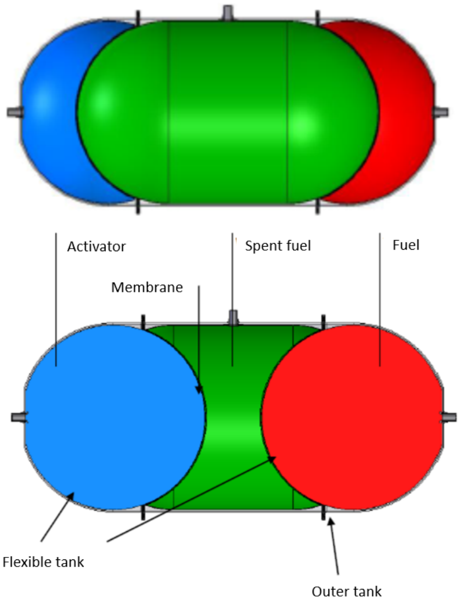

Figure 2.8: Volume-exchange 3 compartment tank system suggested by H2Fuel-systems [64]

In practice more water is added to the process to prevent crystallisation in the reactor. In the scenario of a dry fuel, a recirculation of the fuel cell water and water generation on-board only the volume and weight of the water in the spent-fuel has to be taken into account for the tank volume. In the researches towards sodium borohydride many additional water quantities have been used, all dependent on the type of accelerator and type of reactor. For the calculations of this volume-exchange tank the stoichiometric ratio of the H2 Circular fuel reactor will be used of 2.5, which is representative compared to other researches. For each mol of $NaBH_4$, two mol of H_2O is needed to release the hydrogen and three mol of H_2O is needed to manage the spent-fuel. Three mol H_2O has to be added to the spent-fuel tank volume and weight. Continuing the calculation, 3 times 0.0246 mol or 0.079 mol H_2O has to be added to the volume and weight of the spent-fuel. This results in 1.43 grams and ml per gram of dry $NaBH_4$ stored. In total the volume needed for 1 gram $NaBH_4$ is 0.97 ml, resulting in a spent-fuel volume of 2.14 ml and a weight of 3.17 gram. This means the volume of the spent-fuel becomes more than twice as big and weight more than three times as heavy than the initial fuel. Therefore, in a 2 compartment volume-exchange tank the weight and volume of the spent-fuel becomes critical for the gravimetric and volumetric energy density.

Another option is to use 'slurry' form of 66 wt % $NaBH_4$ in water (fuel 66). The advantage can be that the fuel is easier to handle than the dry fuel, especially in a volume-exchange tank. In this case each gram of 66 wt % solution will result in 1.04 ml in the fuel tank. In the spent-fuel tank this results in 2.09 gram and 1.41 ml mixture of water and $NaBO_2$. In this case the weight of the spent-fuel becomes twice as large and around 40% more voluminous than fuel 66.

The last conceptual option to increase the volumetric energy density is to filter the water out of the spent-fuel. In this concept the spent-fuel is thickened until only 30 $wt.\%$ of water is left in the fuel. This process is comparable to reverse osmosis, as will be discussed later in this chapter, only in this case the water is removed from the substance and not produced like on a normal reverse osmosis system [64].

2.3.3. Ballast integrated volume-exchange tank

As is explained in the previous subsection it might be technological possible to improve the volumetric energy density. It is, however, more challenging to improve the gravimetric density, because the weight can't be 'vanished' when the spent-fuel is still stored on-board. There is, however, another way to look at the weight on the vessel. Since most of the vessels use ballast water to stabilize the vessel and to maintain the desired draught, the weight of the fuels can possibly be used to be integrated in this ballast system, like the diesel tanks on a submarine. The weight addition of the spent-fuel can possibly be compensated by the ballast water, when the tank is integrated properly. It is important to notice that the weight compensation is not possible when no ballast water is needed, such as on a fully loaded inland ship transporting iron ore, and

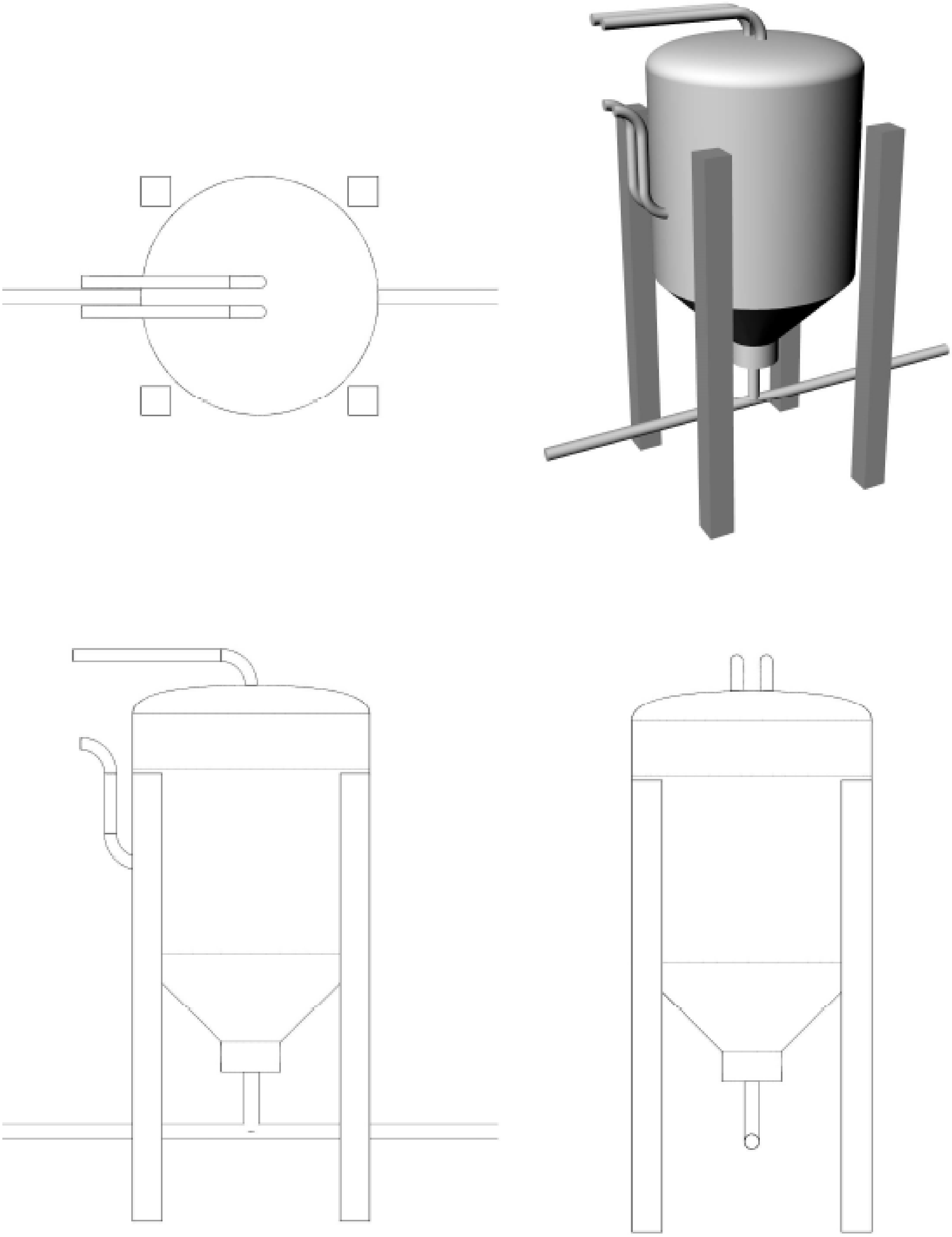

Figure 2.9: Concept of a volume-exchange tank with dry sodium borohydride and solid-liquid spent-fuel

smaller vessels without a ballast water system. It is disputable whether or not the weight and volume of the spent-fuel have to be taken into account when the system density is calculated.

Vessels, which are qualified for a system like this are, for example, big seagoing vessels, which often need ballast water for stabilisation and depth corrections. Two scenario's can be taken into account: an integrated ballast-fuel volume-exchange tank and an integrated fuel and spent-fuel volume-exchange tank. In the first scenario the fuel itself needs to be stored in a separate tank, where no extra space is needed for the ballast water. In the second scenario the ballast-water need to be handled separately from the fuels. An illustration is made to visualise these concepts and give an overview of the feasibility of an implementation of the concept. In this concept a composite tank has been built in the double bottom, to save room on-board of the vessel and to lower the center of gravity of the ship for stability. Storing a dry fuel in a tank like this, would be a difficult technological challenge and. Therefore, a pumpable 'slurry fuel' will be considered in this scenario.

A concept design of an integrated fuel tank has been made as shown in Figure 2.10. In this concept the fuel and spent fuel is stored in a composite tank. A composite tank has been chosen to prevent interaction with the environment. During the trip the ballast water tanks and fuel tanks have to interact with each other, because the fuel tank becomes heavier and, therefore, less ballast water is needed. As can be seen in the figure this system will be more complicated to implement, especially on smaller vessels where the space between the bottoms is limited. Normally a vessel is designed with a minimised amount of ballast water and, therefore, it's unlikely the weight of the fuels can always be compensated. Therefore, this weight compensation is not further analysed in this research. On some specific configurations, however, it could prove beneficial and, therefore, be studied in more detail.

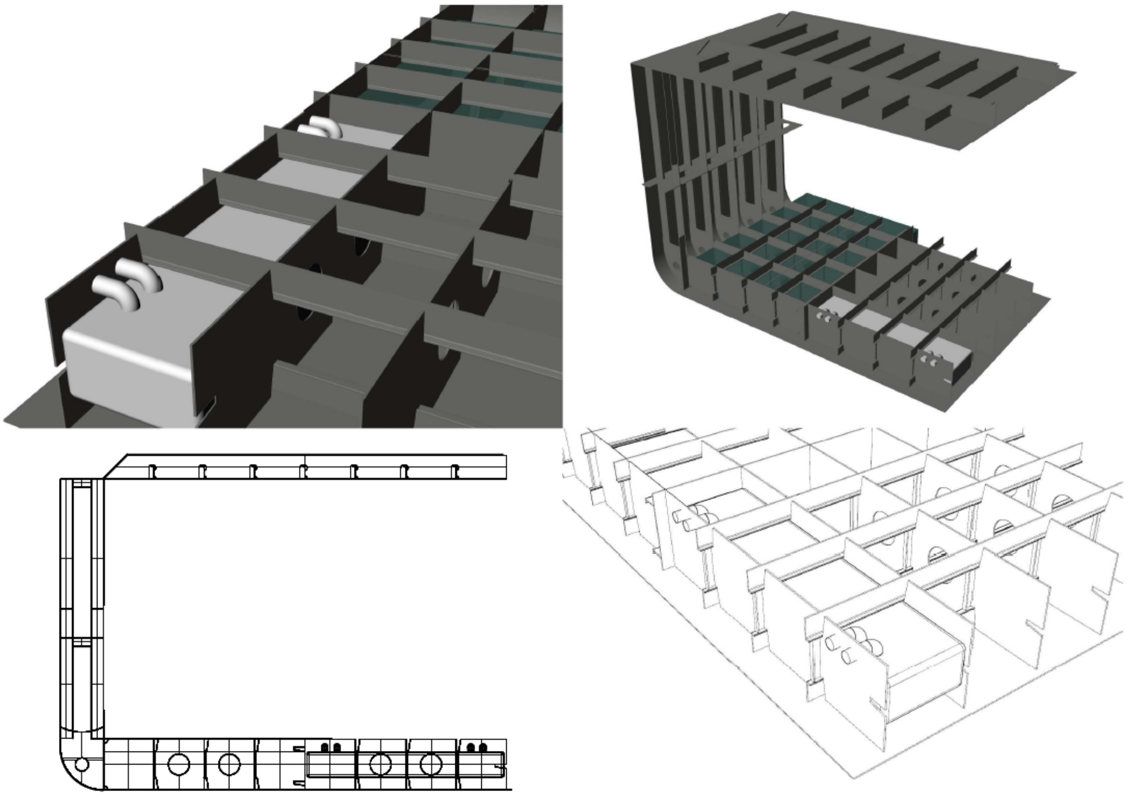

Figure 2.10: Concept of a volume-exchange tank integrated in the double bottom

2.4. Fuel transport and preparation

The fuel handling between fuel-tank and mix chamber is dependent on the installed power on the application. First, the fuels need to be pumped from the fuel tank to the 'pre mixing tank' or service tank. From there the fuel can be injected in the reactor using another pump. Depending on the type of application, water can be added in the service tank from either separate water-tanks, by recycling water from the fuel cell or by making use of reverse osmosis. There is no water addition needed when fuel 30 is used. Hereafter, another pump is needed to transport the spent-fuel to the tank.

2.4.1. Seawater filters

The ultra pure water filter can be used to filter water, which is already filtered or relatively clean. Especially when a dry fuel is used, the amount of water recirculated from the fuel cell is not enough for the process in the reactor. A possible solution is to use water from the environment for this process. This means an extra filter system is needed to clean the environment water. The technology to filter seawater is also known as desalination and is used on applications like: offshore platforms, submarines, sea going vessels and stationary units on land.

The most common technology for desalination is reverse osmosis, making use of a membrane to filter the water. Osmosis itself is a process in which water or another liquid flows through a membrane by itself, caused by the concentration differences of the liquids. The membrane lets only water molecules through and no molecules like salt. Since seawater has a higher concentration the filtered water flows to the seawater naturally. Reverse osmosis turns around this process by creating a higher pressure on the seawater side resulting in a flow to the filtered water. Normally this pressure will be created by pumping the seawater through the filter. The highly concentrated seawater will be discharged back into the sea. James Miller reported in 2003 that an energy demand between 11-60 kJ/kg water is required to produce water using the reverse osmosis technology [42]. Theoretically the energy demand can be reduced, but than the system will become very large and costly.

For each mol of $NaBH_4$, one mol of H_2O is needed from a seawater filter since the other four mol is recirculated from a fuel cell. As has been calculated before, for a 1 MW (potential power from hydrogen) application, this results in a flow of 0.87 mol/s of H_2O or 0.016 l/s. On the MW-scale ,small systems, like used on smaller vessels for drinking water, can be used and are compared in terms of weight and volume in Appendix C.

2.4.2. UPW filter

A filter to separate the impurities of the water is needed to make ultra pure water. Ultra pure water filters are usually used in the semi-conductor industry because of its low electrolytic conductivity. Two methods for the production of ultra pure water are: Electrodeionization (EDI) and mixed bed deionization (MBDI). No chemicals are needed to filter the water in the EDI technology. A specific consumed power of 0.2 - 0.8 $kW/m^3/h$ is, however, required for a system like this. The EDI technology is economically and technologically more effective than the MBDI technology, according to the research of Fedorenko [23]. A disadvantage of this technology is that the water need pretreatment before it can be purified. Still, the MBDI technology is a more traditional way to produce ultra pure water. A disadvantage of using the MBDI technology is that the ion-exchanger need to be regenerated periodically. The MBDI technology is more standard for this scale of applications and is, therefore, used for these calculations. The EDI technology has, however, a high potential in the future to improve the system performance on maintenance and reliability.

To make an estimation of the size and weight of this system ultra pure water filters have been found used in the semi-conductor and pharmaceutical industry. The dimensions and weight are initially scaled with the amount of water produced over time, which can later be related to the amount of power needed for this component. A table of the ultra pure water filters used to calculate the gravimetric and volumetric power density is shown in Appendix C.

2.4.3. Service tanks

A service tank in this system is a separate tank placed just before the mix chamber. Most important reasons to use a service tank is to get the fuels mixed in the correct proportions for the fuel injection and to get a better control of the transport to the mix-chamber. The service tank can also be used to control the temperature of the solution, mix the solution and control the quality just before injection.

The size of the service tank is variable in the design. A bigger service tank will automatically decrease the risk of a full system failure. When, for example, the pump of the fuel tank fails, there is still time to fix this before a system failure when the service tank runs out of fuel. Sizing the service-tank in this system will, therefore, be in a range of a minimum of one-hour fuel-buffer and a maximum of one-day fuel-buffer.

2.4.4. Fuel Pumps

Important parameters for the choice of a pump are the mass flow, the head of pump, the type of fuel, the size and the efficiency. In the case of this fuel handling system first the water solutions will be determined. At solutions like these, most of the time centrifugal and peripheral pumps are used. A list of pumps usable for this system can be found in Appendix C. This results in a gravimetric and volumetric density expressed in weight per mass flow and volume per mass flow.

Stronger pumps will be needed when pumping a slurry like fuel 66. A more suitable pump for these high viscosities will be the displacement pump. Typical displacement pumps used for high viscosity fuels in the maritime sector are screw-pumps and gear-pumps. .

The transportation of a dry fuel will require a pneumatic pump or other powder transfer systems. By making use of a vacuum or by blowing the powder through the pipelines with air or nitrogen the powder can be transported from the fuel tank to the service tank. The powder is mixed with water in the service-tank. An example of a configuration using dry fuel is shown in Figure 2.11. In this configuration the powder and gas is ‘sucked’ to a separator, where it is separated again above the service tank. During transportation, powder is formed in the pipelines. This fine powder can cause some explosions hazards, which has to be taken into account in the design. Another option would be to mix the powder with the water next to the dry fuel tank to exclude or minimize the pneumatic system.

Determining the size of the pump is difficult, because the essential parameters, such as the transportation distance and height difference, vary for each application. Therefore, a minimum distance will be chosen in a feasible first scenario, like two containers on-deck. One container contains the fuels and one container contains the mix-chamber, pumps and service tanks. These containers are placed next to each other.

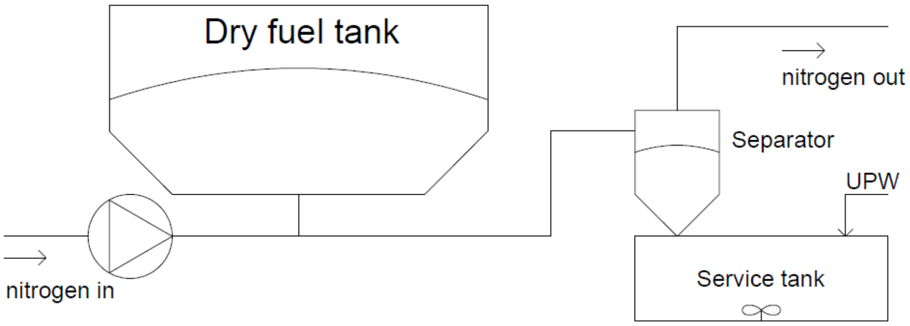

Figure 2.11: Configuration using a dry fuel tank

2.5. Accelerators

Sodium borohydride and water will directly react when they’re mixed together. The speed of this reaction is, however, very low. The size of this reactor will become very large when a high generation efficiency is required and only these two product are mixed in natural conditions. Therefore, it is needed to accelerate this reaction. The three most known methods to accelerate the reaction are the addition of an acid, the use of a catalyst and by operating at high temperatures. These three methods will be discussed in this section.

2.5.1. Acid accelerator

The first method to accelerate the reaction is to add an acid to the process. All Brønsted acids, or acids which can release H^+ protons, can be used for this hydrolysis. Mineral acids like HCL, H_2SO_4, HNO_3, H_3PO_4 and carboxylic acids like $HCOOH$ and HC_3COOH have been tested in different concentrations on its effect on the hydrogen generation efficiency and generation rate [45]. Results of the experiments show that the highest theoretical efficiencies of 97 and 96 % can be achieved by adding a 3 N-HCL solution and H_2SO_4 respectively. An advantage of the carboxylic acids is the high solubility of the spent-fuel in water, but the reaction rates are lower. An example of the reactions in stoichiometric condition using HCL and H_2SO_4 are shown in Equations 2.12 and 2.13 [45].

$$NaBH_4 + HCL + 3H_2O \rightarrow NaCL + H_3BO_3 + 4H_2 \tag{2.12}$$

$$2NaBH_4 + H_2SO_4 + 6H_2O \rightarrow Na_2SO_4 + 2H_3BO_3 + 8H_2 \tag{2.13}$$

In general, the reaction rate becomes higher when the mixture is more acidic. This means that a very concentrated acids will results in a very fast reaction. A half-life smaller then one second is even possible when enough concentrated acid is used. The addition of an acid is, therefore, a interesting method when hydrogen is needed very fast, and in situations where there is no space for a big reactor. By addition of the acid, very high load fluctuations in a compact system can be achieved. Adding an acid is like an homogeneous catalyst, or an activator where the catalyst is used in the reaction. This means some extra weight and volume is needed to store this acid. The mix-chamber becomes, however, relatively small because of the high reaction rates. The acid accelerator is also a challenge from safety perspective like explained further in Chapter 6.

2.5.2. Catalysis

Another way to accelerate the reaction is to make use of a catalyst. The most types of catalysts researched are heterogeneous and containing cobalt, ruthenium and nickel, because of the relatively low cost and high hydrogen generation rates. The tests have been done for different concentrations of $NaBH_4$, $NaOH$ and different temperatures. Until 2011, activities of catalysts have been reported between 1100 and 26000 $mlH_2/min/g$ [17]. The most important parameter influencing the activity is the surface area of the catalyst. A catalyst as a powder will, therefore, increase the activity, which has to be taken into account in the design of the reactor. Looking at the hydrogen storage capacity the efficiency and maximum usable concentration of $NaBH_4$ are of high influence. A higher concentration can result in a blockage in the flow channels and on the catalyst. Concentrations between 10 and 30 $wt\%$ have been reported with a H_2 storage capacity between 1 and 6.3 $wt\%$ [17].

In the research towards different types of catalysts two types are considered; noble and non-noble catalysts. Noble catalysts contain noble metals like platinum and ruthenium and often show the best performance on hydrogen generation activity. These catalysts are, however, rare and expensive and, therefore, a lot of research has been done towards the non-noble catalysts. These catalysts often contain the non-noble metal Cobalt. Research has shown that also high activity can be met using these ‘low-cost’ alternatives [44].

The biggest advantage of the heterogeneous catalyst is that there is no extra fuel needed like with the acid accelerator. The catalyst literally activates the reaction without using the product itself. Furthermore, no tank-volume is needed for the activator and there is no by-product from the activator in the spent-fuel. Reaction rates of the catalyst are much lower than the concentrated acids and, therefore, the mix-chamber becomes much larger to reach the same hydrogen generation efficiency. A practical challenge using a catalyst is the amount of cycles the catalyst can be used. Each cycle or batch, the catalyst will decrease in quality because of pollution. The catalysts need to be recycled or replaced regularly. The challenge for this technology is to find a catalyst with high activity, a low degradation rate and low cost.

2.5.3. Temperature dependence

The hydrogen generation rate will also increase at higher temperatures resulting in the fact that the start-up time of the system will take longer, because the reactor need to heat up before the desired hydrogen generation rate can be reached. This is, however, less critical on most maritime applications and, therefore, this type of accelerator has a potential for the martime industry. Furthermore, the volumetric energy density wil improve and maintenance on the catalyst is avoided in case no catalyst or acid is used. As is illustrated in Figure 2.6, the solubility of the spent-fuel increases at higher temperatures and less water is required to prevent crystallisation in the reactor. For the hydrolysis typical temperatures between 80 en 100 °C can be used to accelerate this process. Even higher temperatures can be met at higher pressures.

Like R. Retnamma said in his research towards the reaction at higher temperatures: ‘The mechanism of this process is highly complex and too complicated to described by a kinetic model within the practical operating conditions’[56]. Therefore, experimental data will be used to determine the temperature influences. The relation between the rate constant and the temperature of the reaction is given by the law of Arrhenius, shown in Equation 2.14.

$$k_{ap}(T) = A_{ap} e^{\frac{-Eap}{RT}} \tag{2.14}$$

Parameters like activation energy (E) and the pre-exponential factor (A) are dependent on the conversion and the viscosity of the product, but also the design of the reactor is of high importance to determine the reaction rate. For usable values in this project experimental results have to be used from other researches for the calculations. However, as can be seen from the equation, if the temperature rises, the reaction rate constant also rises, and the reaction becomes faster at higher temperatures.

Operating at a higher temperature only is a much slower method than using a catalyst or by adding an acid. A very large mix-chamber would be needed for the same hydrogen generation efficiency. Since the reaction is exothermic the mix-chamber can heat-up itself, making this a very low-cost option.

In research also combinations of the accelerators are used. A higher temperature can, for example, be used in combination with a catalyst. In future applications all the accelerators can also be combined. A High temperature for a constant load, a catalyst for the small load fluctuation and the addition of an acid when the load increases rapidly and a great amount of hydrogen is needed on short-term.

2.5.4. Accelerator overview

To size the reactor a inner volume need to be calculated sufficient for the release of the hydrogen and the hydrogen buffer. Just a small reactor would be needed for a certain mass flow when the reaction is very fast. For the same mass flow with a slow reaction speed a much bigger inner volume will be needed. An overview of the advantages and disadvantages of accelerators is given in Table 2.4. In the maritime industry a very fast dynamic behaviour and start-up time is most of the time not needed and, therefore, an acid accelerator might be exaggerated to use on-board of vessels. A better option would be to use a catalyst since it has still a sufficient dynamic behaviour for vessels as is also suggested by H2Fuel-systems.

Table 2.4: Overview of accelerator types

Accelerator	**half-life**	**Advantages**	**Disadvantages**
Acid	<1 min	High reaction speed, High performance on dynamic behaviour, HCL highly available Fast reactor start-up	Safety hazards of high concentrated acids, weight addition + storage, Extra re-fuelling component needed
Catalyst (Cobalt)	~10 min	Catalyst is not 'consumed', low cost, No additional (spent-)fuel	Decrease catalyst efficiency over time, Higher reactor volume and weight,
Temperature	~1 hour	Low OPEX, Low maintenance, Less additional water needed	Slow start-up, Large and heavy reactor

2.6. Reactor types

Multiple reactors will be considered based on existing concepts and applications. Two types of reactors are commonly used; the continuous flow reactor and the batch reactor. Besides these two reactors a multi-purpose reactor will be studied. Most of the time a catalyst in a powder-form on a resin bed is used as accelerator. The catalytic reactor is used for the power density calculations because it is the most promising for the maritime industry.

2.6.1. Continuous flow reactors

The characteristic of a continuous flow reactor are that a continuous stream flows through the reactor. Multiple continuous reactors are know: the Continuous-Stirred Tank Reactor (CSTR), tubular flow reactor and the plug flow reactor [24]. In several researches they use a tube with a catalyst on a fixed bed. A constant stream of a sodium borohydride solution flows through the catalyst bed and accelerates the hydrogen generation. The efficiency of this process is dependent on the length, diameter, the amount of catalyst-powder and the mass-flow of the sodium borohydride solution through the tube. The flow through the reactor can easily be controlled and high pressure fluctuation are prevented [29, 44, 75]. The residence time of the reaction is an important parameter to determine the size of such reactors.

2.6.2. Batch reactors

Another option is a batch reactor where the reaction takes place in 'steps'. First, a batch is inserted in a reactor containing a heterogeneous catalyst or an acid is mixed with the sodium borohydride solution. After the fuel injection the reaction takes places in the reactor until the desired amount of hydrogen is released. The reactor will be emptied thereafter and the process can be repeated. The hydrogen generation efficiency is in this case dependent on the time the solution is kept in the reactor. In practice the efficiency of 100 % will never be reached, but efficiencies above 95% are achievable. Normally the batch reactor is used for: "small production rates, too long reaction times, to achieve desired selectivity and for flexibility in campaigning different product" [29].

The hydrogen flow out of the reactor can be used directly from the reactor to the next subsystem. Disadvantage is that this will result in a highly fluctuating hydrogen generation, because of the reaction characteristics, explained further in this chapter. To ensure a continuous flow from a batch reactor a hydrogen receiver will be needed as a buffer for the hydrogen fluctuation. This receiver can be built inside or outside of the reactor. The reactor will operate at high pressures when this buffer in integrated in the reactor.

2.6.3. Multi-purpose reactor

The advantages of generating and storing the hydrogen can be combined in a multi-purpose reactor. An example of a simplified version is shown in Figure 2.12 [43]. In this configuration a dry sodium borohydride is first mixed with water and stabilizers and then a batch is inserted in the the reactor. In 4 and 5 the batch is recirculated over the catalyst multiple times until the required amount of hydrogen is released. The taps around 6 can now be controlled when the reaction is expired and, thereafter, the new batch can be inserted. In this configuration a H_2-receiver and pre-mixing tank is used to control the process. In a multi purpose reactor this can also be combined in one reactor to safe some space. The flow of hydrogen can be controlled over a wider range when a high pressure reactor is used and, depending on its inner volume, a separate H_2-receiver is not needed anymore. It is important to notice that this increases the size and weight of the reactor but prevents a additional tank in the configuration. An acid accelerator can also be used in another multi-purpose reactor, as is discussed in the second part of this research.

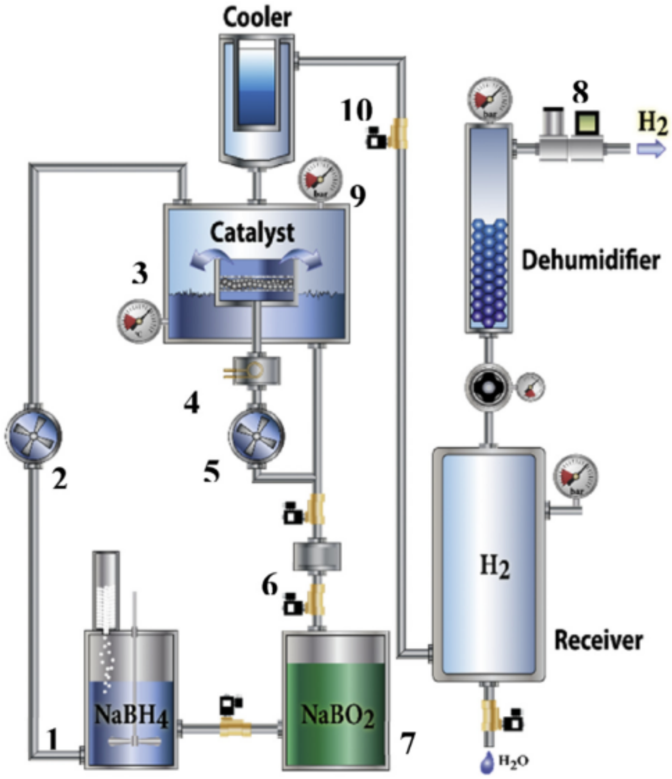

Figure 2.12: A stationary hydrogen generator using a circulating batch reactor [43]

2.6.4. Reactor weight and size

To determine the size and weight of the reactor the inner volume will be calculated. Most reactors used are catalytic batch reactors or a variant of this type. The dimensions and size of the reactor is determined by comparing existing reactors and by a design approximation of a reactor proposed by H2Fuel Systems.

In a batch or multi-purpose reactor the inner volume depends on the hydrogen generation efficiency, the load and the maximum pressure in the reactor. The half-life is 9 minutes (540 seconds) using a cobalt catalyst [9, 64]. This means that after two times the half-life (18 minutes) 75 % of the hydrogen is generated. The generated hydrogen over the time is shown in Figure 2.13 using Equation 2.15

$$C = (1/2)^n \tag{2.15}$$

Where C is the percentage not reacted yet and n the number of half-lifes. From the graph it can be seen that the reaction time increases rapidly for higher efficiencies. Here, a efficiency of 98% will be taken into account, which results in a reaction time 50 minutes for one batch. A total batch-time of 55 minutes is used because the reactor needs time to be emptied after one batch.

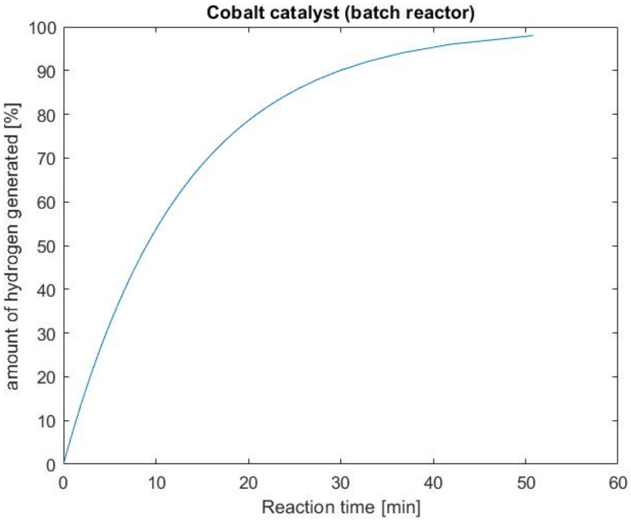

Figure 2.13: Hydrogen generation using a cobalt catalyst in a batch reactor

The inner volume is expressed in l/kWc_{H2} (chemical energy based on the HHV). Using the HHV of hydrogen of 141.7 MJ/kg results in a required hydrogen flow of $7.05 \cdot 10^{-6} kgH_2/s$ for 1 kW and over the 55 minutes a total of 0.024 kg in one batch. To produce this weight of hydrogen a total of 0.38 kg or 0.27 l of water plus sodium borohydride together is needed. This will be the inner volume of the liquid part in a 1 kWc reactor.

The hydrogen released from the reaction does not need to leave the reactor immediately when the reactor is designed for higher pressures. The pressure and the volume needed to stored the hydrogen can be approximated by the ideal gas law shown in Equation 2.16

$$\frac{PV}{T} = nR \tag{2.16}$$

Where n is the number of mol, V the volume in m^3, T the temperature in Kelvin, P the pressure in Pascal and R the gas constant (8.314 $J/(K \cdot mol)$). In this case it is assumed that one full batch can be stored in the reactor. The effect of the temperature at different pressures is shown in Figure 2.15. A reactor inner volume around 3.8 l is needed when a reactor pressure of 100 bar is used together with the possibility to store one batch.

A list of high pressure fixed bed reactors is made comparing the inner reactor volumes to generalise the total dimension and weight of the reactors. This is shown in Appendix C. This results in a range of 27.5 - 101.2 $l_{system}/l_{inner volume}$ and 30.9 - 132.3 $kg_{system}/l_{inner volume}$. This means that the reactor volume is at least 27.5 times as big as the inner volume. This is, however, not a representative value since the reactor will not scale linear like also illustrate in Figure 2.14. Here it can be seen that the ratio between inner volume and reactor size decreases when the power of the reactor increases.

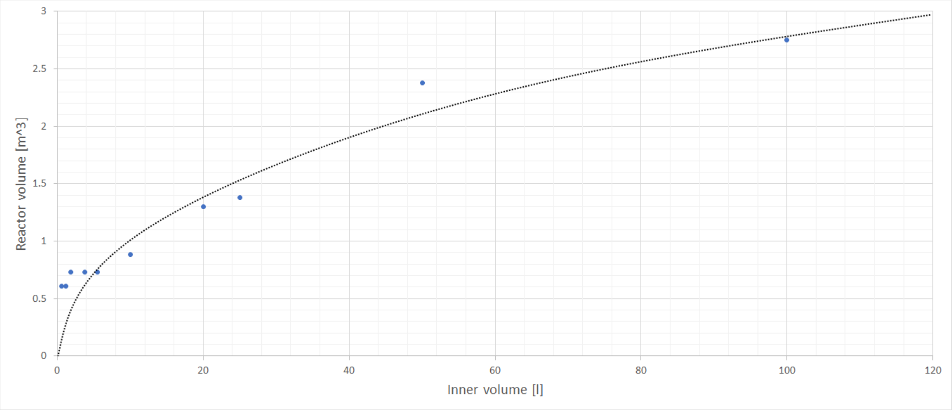

Figure 2.14: Relation between the inner reactor-volume and total reactor-volume based on a batch reactor database in Appendix C

Another method to estimate the size of the reactor is shown in Figure 2.16. Here the dimensions are estimated based on a 1000 l inner volume reactor with a double wall structure for the pressure and some space defined beneath and above the reactor for pipelines, dehumidifier, construction etc.. This method results in a reactor three times as big as the inner volume. For the system size estimation a range of 2 to 6 times the inner volume is used, based on these estimations.

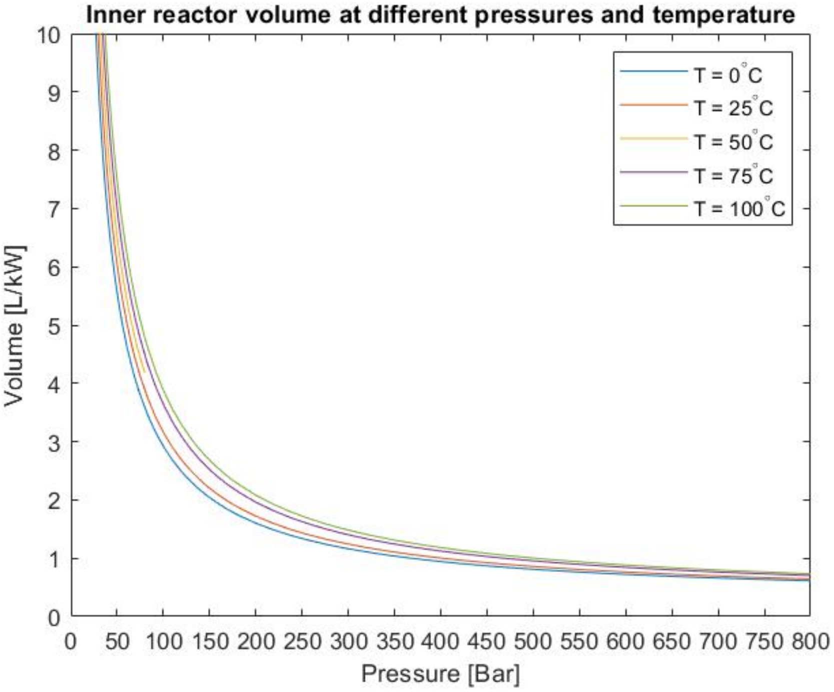

Figure 2.15: Inner volume of a multi-purpose reactor with a cobalt catalyst in [L/kW] for one batch of hydrogen storage and liquids

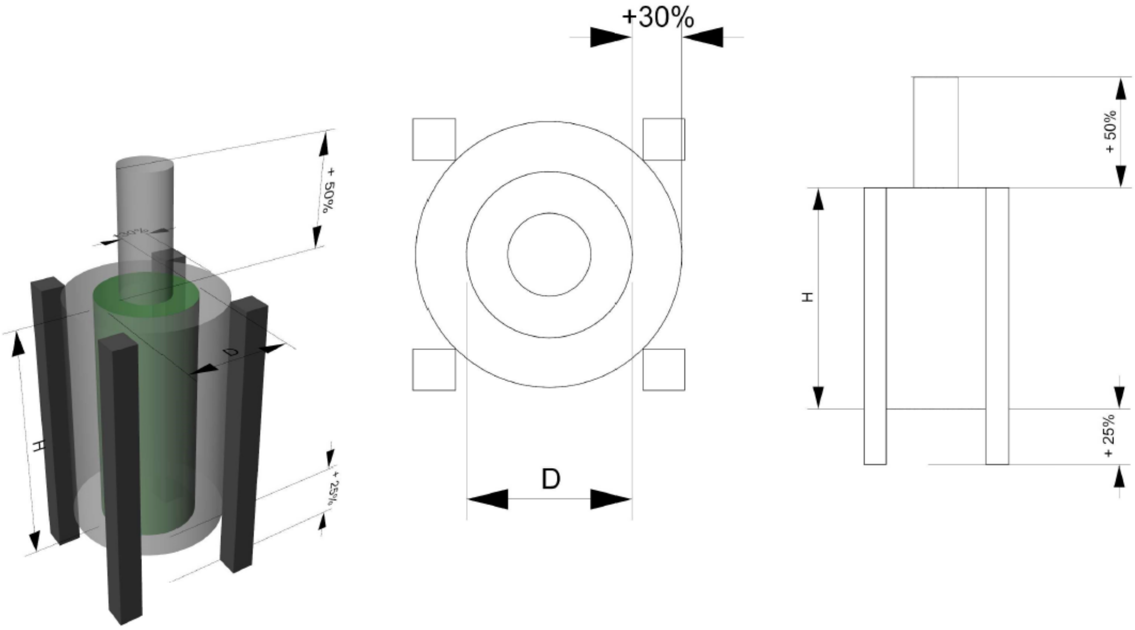

Figure 2.16: Reactor dimension in the range of a 1000 L inner volume catalytic reactor

2.7. Fuel handling system overview

All components of the fuel handling system have now been studied on its dimensions and weight. The volumetric and gravimetric energy and power density will now be summed up and analysed. Two scenario's will be taken into account to determine the range of the densities. In Figure 2.17 and 2.18 the most volumetric (scenario 1) and less volumetric (scenario 2) configurations are shown. In both scenarios all minimum and maximum volumes and weights are taken into account resulting in a volume and weight range of the system. In the first and most volumetric configuration all water needed for process is stored on-board in separate tanks. This means a Fuel 30 and a unfiltered spent-fuel is used. In the second configuration all options to make the system more compact are taken into account. This configuration is much more complex than the first configuration, but the energy density will be much higher because the water is not stored on-board. Such as illustrated in Figure 2.18 a part of the water is produced on-board using reverse osmosis and the other part is recycled from the fuel cell. After the reactor the spent-fuel is filtered in order to separate the water and to make the spent-fuel more compact.

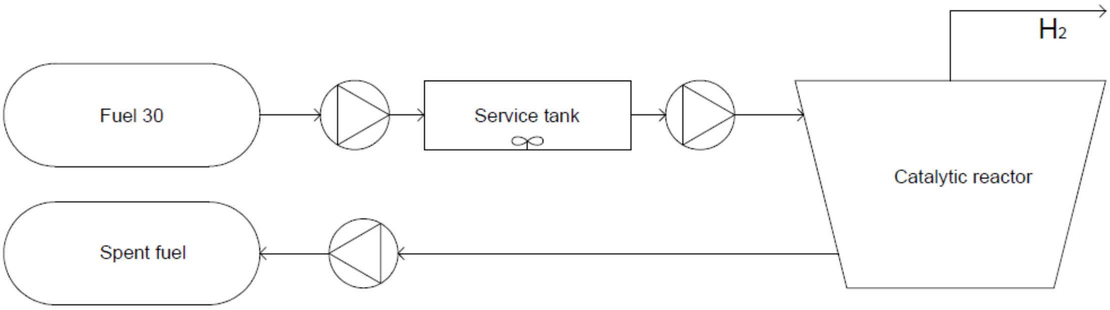

Figure 2.17: Scenario 1: separate tanks, Fuel 30 and unfiltered spent-fuel

Table 2.5: Energy densities of the Fuels

Overview of fuel densities (including reactor efficiency)				
	min [kg/kg H2]	max [kg/kg H2]	min [l/kg H2]	max [l/kg H2]
Dry Fuel	4.79	5.21	4.47	4.87
Fuel 30	16.19	17.63	11.56	12.59
Fuel 50	10.37	11.29	7.97	8.68
Fuel 66	7.25	7.90	6.31	6.87
Spent-fuel	15.19	16.63	11.68	12.79
Spent-fuel (filtered)	11.90	12.95	5.95	6.48
UPW (5)	11.40	12.41	11.43	12.45

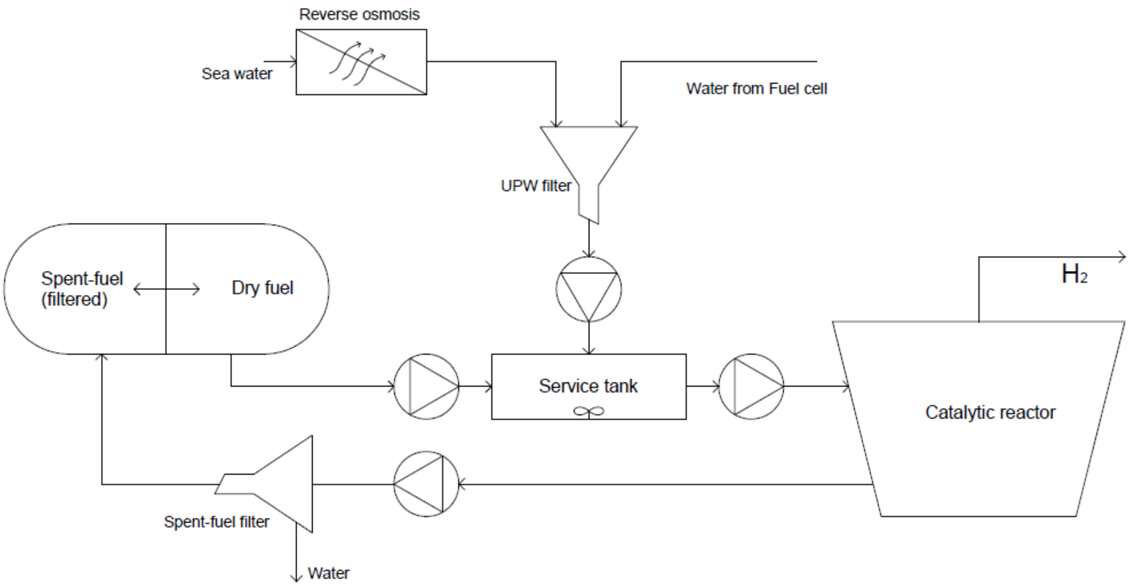

Figure 2.18: Scenario 2: Volume-exchange tanks, dry fuel, filtered spent-fuel, reverse osmosis and a UPW-filter

2.7.1. Energy and power density

An overview of the results in gravimetric and volumetric energy density is given in Table 2.5 for the fuel types and in Table 2.6 for the tank systems. The possible components related to the power density are summed up in Table 2.7. The size and weight of the reactor will be the most significant part of this subsystem because it's much heavier and bigger than the other system components. For both scenario's the power densities are close to each other. The reactor size and weight will be significant in all cases looking at this subsystem only.

With the results of these components a configuration can simply be calculated by summing up the required components from the tables. Both scenarios are summed up in Table 2.8 and 2.9. These results will be used in Chapter 5 where all weights and volumes of the drive train are included.

2.8. Conclusion

The fuel handling system on sodium borohydride can be be implemented using many types of fuels and configurations. In the most simple configuration all water needed to release the hydrogen from sodium borohydride is stored in the fuel or spent-fuel. The water used in this process will, however, lead to a high volume and weight of the fuels. The energy density of this system is in the range of 32 - 39 kg/kgH_2 and 30 - 45 l/kgH_2. A 30 wt.% $NaBH_4$-solution and an unfiltered spent-fuel is used in this case.

There are several ways to make the system more compact when volume or weight are becoming critical elements in the design of such a system. A volume-exchange tank will increase the energy density when both,

Table 2.6: Energy densities of the Tank systems

Overview of tank weights and additional volume				
	min [kg/kg H2]	max [kg/kg H2]	min [l/kg H2]	max [l/kg H2]
Seperate tanks				
Dry	0.27	0.88	1.34	3.90
Fuel 30	0.69	2.27	3.47	10.07
Fuel 50	0.48	1.56	2.39	6.95
Fuel 66	0.38	1.24	1.89	5.49
Spent-fuel	0.70	2.30	3.50	10.23
Spent-fuel (filtered	0.36	1.17	1.78	5.18
UPW	0.69	2.24	3.43	9.96
Volume-exchange tank				
Fuel 30 / Spent-fuel	1.16	2.77	4.62	11.33
Dry / spent-fuel (filtered)	0.45	1.07	1.79	4.38

Table 2.7: Power density of the subsystem components

Fuel transport, preparation systems and catlytic reactor				
	min [kg/kW_chem H2]	max [kg/kW_chem H2]	min [l/kW_chem H2]	max [l/kW chem H2]
Reverse osmosis	0.053	0.404	0.101	0.786
UPW-filters	0.015	0.040	0.037	0.155
Service tank	0.295	7.720	0.211	5.514
Pumps				
Dry	0.005	0.016	0.016	0.019
Fuel 30	0.010	0.033	0.033	0.038
Spent-fuel	0.010	0.034	0.034	0.040
Reactor				
Inner volume			3.7	4.1
Cat. Reactor	7	24	7	24

Table 2.8: Energy density range of scenario 1 and 2

	min [kg/kg H2]	max [kg/kg H2]	min [l/kg H2]	max [l/kg H2]
Scenario 1	32.77	38.82	30.22	45.68
Scenario 2	12.34	14.02	7.74	10.86

Table 2.9: Power density range of scenario 1 and 2

	min [kg/kWch H2]	max [kg/kWch H2]	min [l/kWch H2]	max [l/kWch H2]
Scenario 1	7.79	32.19	7.77	30.00
Scenario 2	7.92	33.07	8.04	31.77

the fuel and spent-fuel are stored in the tank. A more concentrated $NaBH_4$-solution or spent-fuel results in a more compact and complex system. The water needed for the reaction has to be produced by the fuel cells, or by making use of reverse osmosis on-board the vessel. The most compact and light configuration can be realized by making use of: a dry $NaBH_4$-powder, produce the water on-board, partly filter the water out of the spent-fuel and by implementing a volume-exchange tank. The energy density of this configuration is in the range of 12 - 14 kg/kgH_2 and 7 - 11 l/kgH_2.

The results of the power density of the configurations are close to each other. Most important factor in the power density is the size of the reactor. The other components in the system are relatively small. For most applications in the maritime industry a catalytic reactor is the most logical choice. The power density lies in a range of 7 - 32 l/kW, expressed in the potential chemical energy in hydrogen.

3

Fuel cells

From the fuel handling system the chemical energy in the hydrogen needs to be converted to electrical or mechanical energy. An option, which receives many attention these days, is the use of fuel cells systems. A fuel cell converts the chemical energy in a fuel like hydrogen directly to electrical energy [48]. The developments in the fuel cell technologies are resulting in an increase of technical and financial feasible applications on-board of vessels. Important advantages using a fuel cell as a prime mover are the high efficiencies, low maintenance and the reduction in noise and vibrations. Furthermore, NO_x-formation is highly reduced in comparison with the combustion engine when a low temperature fuel cell is used.

Another option would be to use an internal combustion engine where hydrogen and diesel for ignition can be combined. The mechanical energy from the engine can directly be used for propulsion, and for electricity generation on-board. Implementation of this system using sodium borohydride as an energy carrier would be a interesting option when converting an existing diesel application to a hydrogen application, using the same engine. In this case the diesel engine need to be adjusted to a duel fuel engine, in order make the use of hydrogen gas possible. NO_x-formation would, however, still be high in comparison with the fuel cell. Therefore, this type of prime mover is not included in this research.

In this chapter the opportunities of different types of fuel cells using hydrogen as a fuel are discussed. First, the working principle of the fuel cell systems are explained and a comparison between different types is made. Thereafter, an estimation of the volumetric and gravimetric power density is provided to conclude the total system volume and weight in Chapter 5.

3.1. Working principle of a fuel cell

The fuel cell converts chemical energy to electrical energy through an electrochemical reaction. Different types of fuel cells exist characterised by the electrolyte used in the cell [19]. The basic principle of the fuel cell is schematised in Figure 3.1 [48]. Here the "reactant transport" into the fuel cell is presented in (1), the "electrochemical reaction" in (2), the "ionic conduction" through the electrolyte and "electric conduction" through the external circuit in (3) and the "product removal" in (4) [48]. A fuel cell consist of a anode side "where electrons are removed from a species" and a cathode "where electrons are added to a species" [48]. In between the anode and cathode an electrolyte is used to make it possible to let ions through and to prevent electrons to flow though. As shown in Figure 3.1 [48] the fuel is inserted at the anode side and oxygen is inserted at the cathode side.

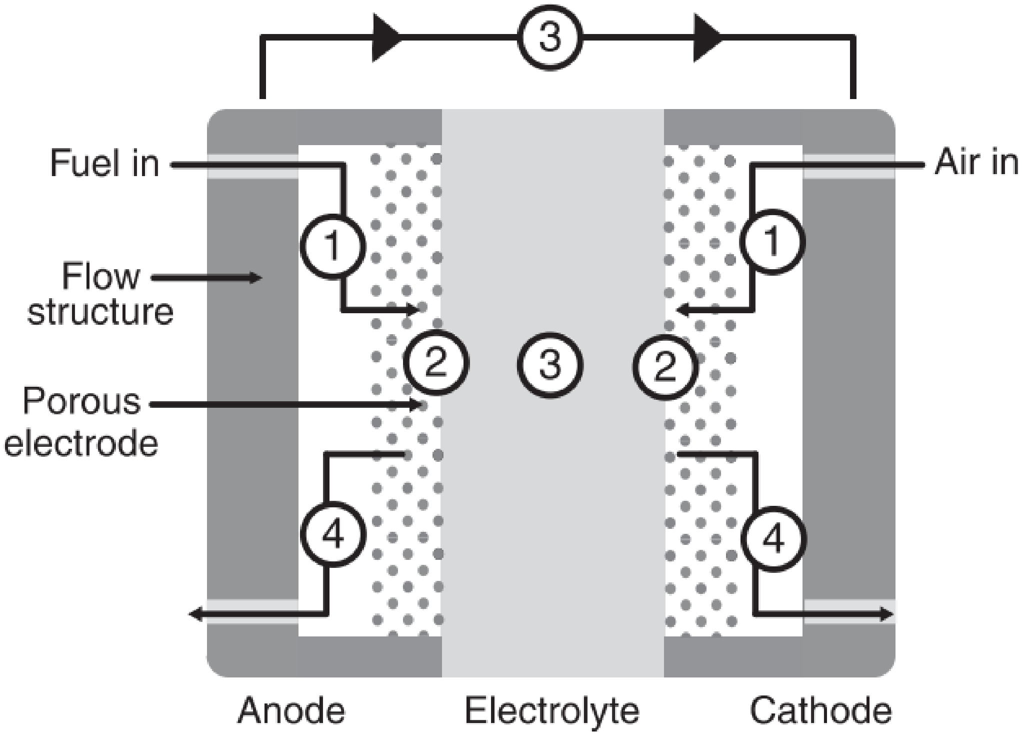

Figure 3.1: Working principle of a fuel cell schematised in a cross sectional view [48]

Depending on the type of fuel cell the product of the electrochemical reaction is formed at the anode or cathode side. In a PEMFC the electrons from the hydrogen are separated in a electrochemical reaction at the anode side. The electrons are guided around the electrolyte used for the load on the fuel cell and the protons are flowing through the electrolyte. The reactions taking place in a commonly used PEMFC are shown in Equations 3.1, 3.2 and 3.3.

$$Anode: 2H_2 \rightarrow 4H^+ 4e^- \tag{3.1}$$

$$Cathode: O_2 + 4H^+ + 4e^- \rightarrow 4H_2O \tag{3.2}$$

$$Total: 2H_2 + O_2 \rightarrow 2H_2O \tag{3.3}$$

The emission of the fuel cell is water when hydrogen is used as a fuel. Since H_2O is also needed for the hydrolysis in the reactor this water can be recirculated. The maximum amount of water, which can be recirculated to the service-tank, can be concluded from Equation 3.3 and 3.4. For each mol of $NaBH_4$ there is 5 mol H_2O required and from the generated hydrogen in the reactor ($4H_2$) the fuel cell produces $4H_2O$. This means there is 1 mol extra H_2O needed when a dry fuel is used.

$$NaBH_4 + (2+3)H_2O \rightarrow NaBO_2 + 4H_2 + 3H_2O \tag{3.4}$$

In Figure 3.1 [48] only one cell of a fuel cell stack is demonstrated. In a stack multiple cells are combined. By connecting the cells in series, the voltages are summed up and in this way the system voltage is determined by the number of cells. In the stack flow-channels control the hydrogen and oxygen flow. The fuel and air processing before the stack are a large part of the total weight and volume of the system. This also depends on the type of fuel cell and the type of fuel. Many fuel-processing is required when there are impurities in the fuel, especially using fuel cells which are sensitive these impurities.

Five well known types of fuel cells are: Phosphoric Acid Fuel Cells (PAFCs), Polymer Electrolyte Membrane Fuel Cells (PEMFCs), Alkaline Fuel Cells (AFCs), Molten Carbonate Fuel Cells (MCFCs) and Solid-Oxide Fuel

Cells (SOFCs). A Sodium borohydride solution can also be used in a ‘special’ type of AFC, where the solution is directly used in a direct borohydride fuel cell (DBFC). Besides the hydrolysis of sodium borohydride in a reactor this DBFC is also extensively researched. The DBFC is still in an initial development phase and suffers from high cost and low durability [17]. Therefore, this fuel cell is not be included in within this master thesis. This technology is, however, important to keep an eye on because it could possibly change the configuration using sodium borohydride in future applications.

The most important performances of a fuel cell can be concluded from a current-voltage plots, as is illustrated in Figure 3.2 [25]. This figure shows the overall performance of the cell in terms of current density and voltage delivered by the cell including the losses in the cell. The open circuit voltage is the theoretical voltage of the fuel cell. The Nernst loss is due to the concentration change of the fuel and air, the internal resistance due to the ohmic resistance of the components and the polarization loss due to the activation in the electrochemical reaction. The difference between the terminal voltage where all the losses are added and the theoretical voltage results in the total loss at different current densities. This is also the energy converted to heat instead of electrical energy. The heat can partly be used in the fuel processing or on external systems on-board. "The current supplied by a fuel cell is directly proportional to the amount of fuel consumed. Therefore, as fuel cell voltage decreases, the electric power produced per unit of fuel also decreases. In this way, fuel cell voltage can be seen as a measure of fuel cell efficiency" [48].

The power density can be determined by multiplying the voltage with the current density. In Figure 3.2 [25] also the power density of the cell is shown. At lower current densities the power density is lower, but the efficiency is higher. At higher current densities, above the maximum power, both efficiency and power density drops, partly because of the increasing concentration losses. Therefore, it is not advisable to operate at higher current density than the maximum power that can be delivered. The cell performs better in part-load from efficiency point of view. The cell does, however, also have a minimum operating point. The balance of plant can’t control the low flows to the stack anymore when the cell operates beneath this point, causing an unbalanced flow trough the cells. As a result there is always a minimum load determined in the design of a fuel cell module.

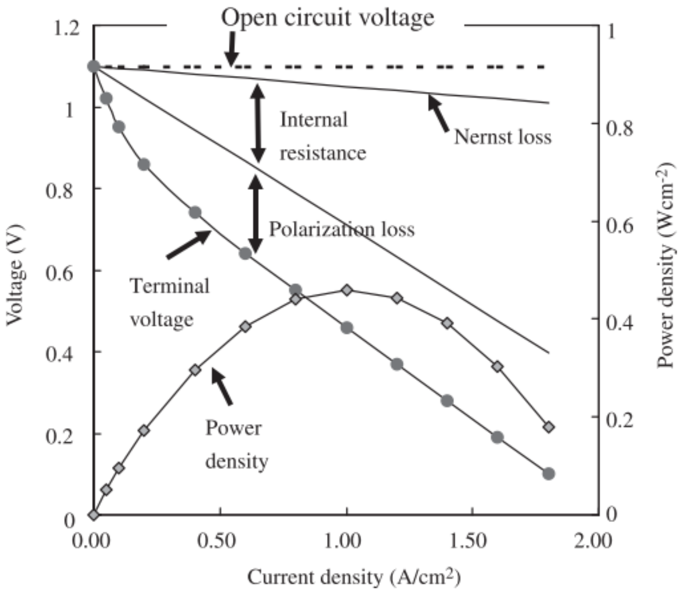

Figure 3.2: Relation between V-I characterization and voltage loss [25]

3.2. Types of fuel cells

Three types of fuel cells will be further analysed: The high and low temperature PEMFCs and the SOFCs. These fuel cells can all run on hydrogen released from the reactor and does have a high potential to be a compact and/or efficient solution.

3.2.1. LT-PEMFC

The LT-PEMFC is a commercially developed type of fuel cell at this moment. The PEMFC consist of a porous anode and cathode and "because of its low temperatures, platinum-based materials are the only practical catalysts currently available"[48]. A disadvantage of this catalyst is the high cost of the platinum. The fuel cell operates on hydrogen and oxygen unless a reformer is used. Due the low temperature, the cell is very sensitive to impurities, especially on carbon monoxide. Therefore, the total system of a LT-PEMFC can become more complex and the power density will decrease when less pure fuels are used because purification is required.

The system has the highest power density and performs well in dynamic behaviour in comparison with the HT-PEMFC and SOFC. Moreover, high system efficiencies can be reached between 50 and 60% in LHV. The efficiency and the power density are correlated; when a higher density is required efficiency will decrease. Therefore, light and heavy duty systems are available on the market. For maritime applications, volume and weight of the prime mover are less significant parameters than, for example, in the automotive industry. Therefore, a heavy duty application with a high efficiency will most of the time be the most logical choice. The cost of a very compact system are high and it can, therefore, be more lucrative to choose a cheaper, less compact, system with a higher efficiency. Looking at the systems volumetric and gravimetric power density it would not be reasonable to take the highest efficiency of 60% and also the most compact system.

During the life time of the fuel cell the efficiency will decrease slowly, mainly because of the degradation in the cell. The amount of degradation is dependent on the type of fuel, the quality of the fuel and air, and the operating conditions. The stack need to be refurbished or replaced when the efficiency has been dropped to a limit defined by the manufacturer. The time between this operations is the lifetime of the stack. A life-time of a heavy duty module is most of the time designed for applications with many running hours, like on-board of vessels.

3.2.2. HT-PEMFC

Operating at higher temperatures, like with a HT-PEMFC, partly compensates the disadvantages of a LT-PEMFC. An important advantage is that the fuel handling becomes easier, because it has a higher tolerance to impurities in the fuel. The temperatures of the HT-PEMFC are varying between 100 and 200 °C. HT-PEMFC can reach efficiencies between 35 and 45 % at this moment, which is much lower than the LT-PEMFC. Efficiency losses in the fuel processing are, however, lower because of the less complex fuel processing system.

A HT-PEMFC will become interesting when the hydrogen from the reactor is not pure enough for fuel reforming or the fuel processing becomes to voluminous and heavy when a LT-PEMFC is used. There are, however, barely impurities in the hydrogen when ultra pure water and 98 % pure sodium borohydride is used in the reactor. The university of Gent has researched the impurities in the hydrogen from the reactor. Impurities are mostly helium atoms, released from the impure sodium borohydride [64].

3.2.3. SOFC

The solide oxide fuel cell (SOFC) operates at a much higher temperature in the range of 500 to 1000 °C. The fuel, or in this case the hydrogen, is inserted on anode side and also the water (steam) is formed at the anode side. The oxygen is inserted at the cathode side. The electrochemical reactions taking place are shown in Equation 3.5 and 3.6.

$$Anode: H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{3.5}$$

$$Cathode: \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \tag{3.6}$$

The electrode is a oxygen conducting membrane and because of the high temperatures a solid ceramic electrolyte is used. An SOFC does not only run on hydrogen but can also operate on hydrocarbons.

The voltage normally decreases when a higher temperature is used in a fuel cell and, therefore, the thermodynamic efficiency also decreases. This does not mean the total efficiency drops because at a higher temperature the ohmic losses decreases. Normally, the total efficiency of a fuel stays the same or even increases at higher temperatures.

An Advantage of the SOFC is the fuel flexibility, because of the high temperatures and steam formation in the anode. Moreover, high efficiencies can be met between 55 and 65 % using the LHV. Even higher efficiencies can be met when waste heat recovery is applied. It becomes easier or more lucrative to implement a waste heat recovery system because of the high temperatures. Application of waste heat recovery can for example be seen in combination with a gas turbine. Efficiencies above 75% can be met by making use of waste heat recovery in combination with a high temperature fuel cell [48].

3.2.4. Fuel cell comparison

Besides the open circuit plot many other performances of the fuel cell can influence the design choice of this prime mover [48]:

1. Relative cost
2. Power levels
3. Lifetime
4. Tolerance for cycling
5. Technological maturity
6. Physical size
7. Sensitivity for fuel impurities
8. Emissions
9. Safety aspects
10. Emissions
11. Safety aspects
12. Efficiency
13. Availability
14. Scalability

An overview of the performance parameters of each type of fuel cell, based on existing systems, is shown in Table 3.1 [69]. The typical characteristics of the LT-PEMFC, HT-PEMFC and SOFC are compared to each other here. Besides the total system density more conclusions from this table can be drawn. The life time is expected to be the highest for the HT-PEMFC, because the temperatures are relatively low and the cell is less sensitive for impurities and, therefore, the decrease in efficiency will take longer. According to the DOE a lifetime of 60000 hours can potentially be achieved. ALthough, many improvements still need to be made to reach this goal. [58, 59]. The life time of an SOFC is somewhat lower, mainly because of the high temperatures affecting the materials in and around the fuel cell. A typical lifetime for a LT-PEMFC for automotive applications is 5000 hours where even 40000 hours can be met in stationary test conditions [67]. The impurities in the air or in other components of the system affecting the durability of the system significantly.

The start-up time increases when operating temperatures are increasing, because the cell need to reach its operating temperature. To accelerate this process usually a start-up burner is used, especially for high temperature fuel cells. The loss in energy has to be taken into account in the start process of the cell. The average efficiency will go down when a system has to start often. It is, therefore, not advisable to use a high temperature cell, like a SOFC, when the engine has to start frequently. Therefore, the SOFC is barely used in the automotive industry and is used more as a stationary system running continuously. A more continuous demand in the maritime industry is more common, especially on applications on a higher scale and long trips.

The dynamic behaviour of the cells are presented in load transient where the LT-PEMFC performs better than the HT-PEMFC and SOFC. The dynamic behaviour of a fuel cell has always been a challenge. The acceleration, deceleration and load fluctuations can affect the life-time of the fuel cell negatively and, therefore, auxiliary systems like capacitors or batteries may be needed to improve the performance of the systems dynamic behaviour. The sizing of this system together with the fuel cell sizing need to be estimated carefully, which will be done in the second part of the research. Using a higher temperature fuel cell will also mean more or heavier auxiliary systems will be needed to achieve the same dynamic behaviour.

The cost of fuel cells are still very high because of the relatively young and small scale market. Especially in comparison with the diesel engine it is hard to find a financial attractive case these days, but the expectations are that the cost of the systems will decrease. Developments in efficiency and lifetime will, however, lead to lower operational cost of the system. At this moment, the LT-PEMFC is lower in cost than the other fuel cells, because of the simplicity of the system and the maturity of the technology. The higher efficiency of an SOFC, on the other hand, can lead to a decrease in the operational cost and might be a better option in some of the applications, looking at the total cost over the lifetime of the system. The Technology Readiness Level (TRL) shown in table 3.1 [69] are based on the systems already implemented in maritime industry only. In other markets the SOFC has a higher level than the HT-PEMFC.

Table 3.1: Characteristics of a LT-PEMFC, HT-PEMFC and SOFC [69]

	LT-PEMFC	**HT-PEMFC**	**SOFC**
Operating temperature (°C)	40 - 80	150 - 180	500-1000
Electrical efficiency (LHV)	50-60	35-45	50-65
Fuel purity required	99.999% H2	CO<3%	Light hydrocarbons (S<20 ppm)
Gravimetric power density (W/kg)	250-1000	-	8.0-80
Volumetric power density (W/l)	300-1550	-	4.0-32
Life time	5 to 20k hours	10 to 60k hours	10 to 40k hours
Start-up time	<10 seconds	10 to 60 minutes	30 minutes to hours
Load transients (0 to 100%)	<5 seconds	2-5 minutes	<15 minutes
Capital cost today ($/kW)	>1000	4000-4500	3500-15000
Technology Readiness Level (TRL)	8	7-8	5-7
Cooling	Water cooling	Water cooling	Air cooling
Waste heat recovery	-	-/+	++

3.3. Developments in the fuel cell technology

Development in cost and efficiency is always an important topic for the fuel cell technology. Experimenting with new types of materials or a more efficient balance of plant are continuously resulting in better performances on efficiency and power density. Furthermore, the research towards more reliable and cheaper systems are increasing. An example is the development in decreasing in operating temperature of a SOFC to make it possible to use other materials and increase the life time of the cell [25]. Like already shown in Table 3.1 cost are to high at this moment, mainly because the technology is not fully commercialised yet. To make the fuel cell better competitive with other engines like the internal combustion engine the cost has to be lowered.

The department of energy set targets to improve performances like mentioned above. Peak efficiencies of the LT-PEMFC are targeted on 65 %, the life time on 8000 hours and a cost on 40 $\$/kW$ in 2020 for the automotive industry. Especially the cost will be a challenge and will only get close to the targets when a high-production volume can be realised [67].

3.4. Conclusion

Fuel cells have many advantages for the maritime industry. The compact, efficient modules are improving the energy and power density of the system. The emission of NO_x can be decreased significantly by using a low temperature cell in comparison with an ICE. When hydrogen is used as a fuel also the CO_2 and SO_x emissions are eliminated. Other advantages are: high performance in part-load and a silent system.

The LT-PEMFC, HT-PEMFC and the SOFC are considered for this drive train . The PEMFCs results in a compact and efficient solution, operating at low temperatures. The life-time of this fuel cell is proven to be sufficient for the use in the maritime industry. The LT-PEMFC is very sensitive to impurities in the fuel, which is partly solved by using a HT-PEMFC. The efficiency of a HT-PEMFC is, however, much lower and the system is less compact. The LT-PEMFC would be a better solution for a sodium borohydride solution because the quality of the hydrogen from the reactor is high enough.

The SOFC operates at higher temperatures. In general a much bigger system is required for a module like this. The efficiency of the SOFC, however, is higher than a PEMFC and waste heat recovery can be implemented more easily. Depending on the application both systems has its advantages and disadvantages. One of the most import factor is the combination of the power density and the energy density of the system.

4

Other system components

The prime mover and fuel handling system in the drive train have been analysed. In this chapter the remaining components in between the prime mover and the propeller will be discussed. Many attention is drawn to a fuel cell configuration and, therefore, the electrical grid becomes a logical step to discuss next. The electrical energy on a vessel will be converted to use for propulsion via an electrical motor or to use for other purposed, such as auxiliary systems and hotel requirements. For the components in this chapter the efficiencies will be analysed.

4.1. AC and DC power grid

The power management system controls the power supplied to the loads, to keep a nominal voltage and frequency, to prevent inefficiencies and dangerous situations. Depending on the supply of the power and the type and amount of loads, the system can become very complex, including several transmissions [72]. For now, this system is simplified to the prime movers and one or two loads. Most of the current systems are using an AC-bus to connect the suppliers and users. Since most systems are compatible on AC, and diesel generators most of time produce an AC current, an AC-bus seems the most logical choice. Throughout history the AC-grid on-board of vessels became popular. It was safe and electricity was easier to transport over long distances in comparison with a DC-grid [33]. Furthermore, the electrical motor and most of the users require AC. Therefore, less or less complex conversion steps, are needed for these types of configurations. A typical AC-configuration on-board of a vessel is shown in Figure 4.1 [52].

The DC grid is becoming more attractive nowadays, because of new technological advantages [62]. New configurations focussed on sustainable sources and new ways to store electrical energy are being developed. Systems such as hybrid AC/DC or full DC power systems are of high interest. A typical DC-configuration is shown in Figure 4.2 [52]. In these configurations the power is generated by multiple diesel generators producing AC power. With an AC-grid the power to an induction or synchronous motor first needs to be converted to DC in a rectifier, and than have to be converted back to AC in order to control the speed of the electrical motor. This is not the case for a DC-grid, where the power only has to be converted one time to AC, as can be seen in the figures. The other crew-related loads, like the hotel services, need to be switched to AC using a power transformer on a DC-grid. The power transformer is a heavy and a cheap solution, but relative small since in many cases these loads are very small in comparison with the propulsion.

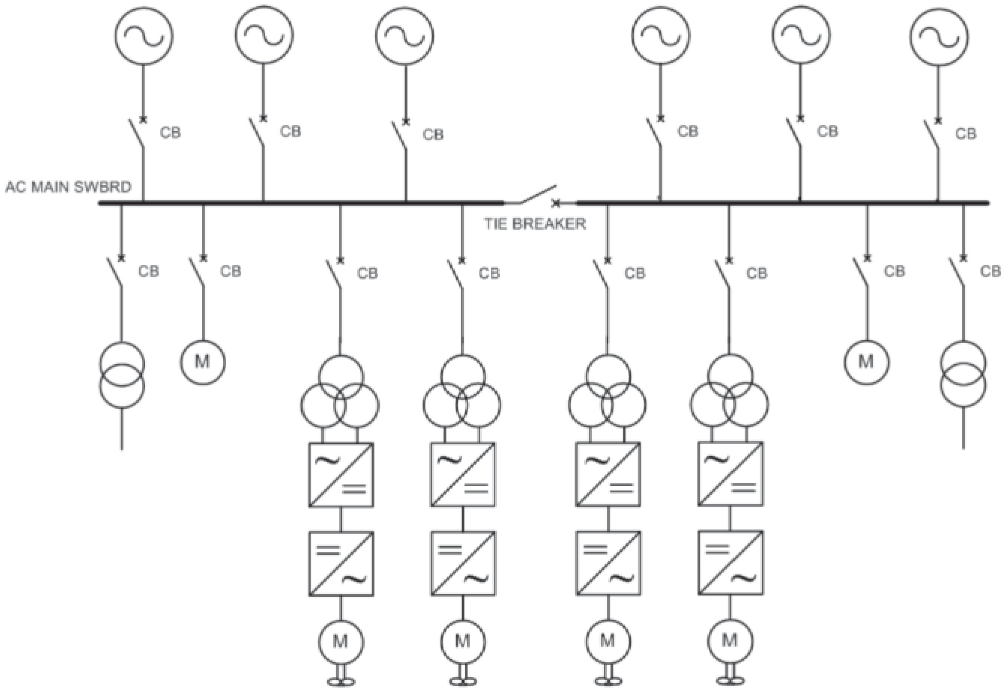

Figure 4.1: Typical AC-configuration [52]

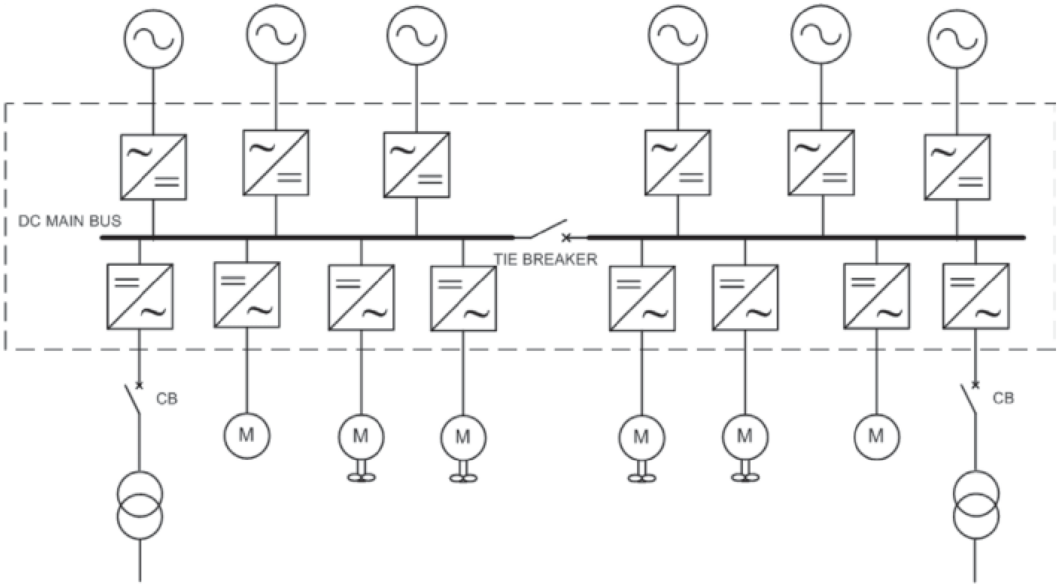

Figure 4.2: Typical DC-configuration [52]

A DC-grid can be advantageous looking at the efficiency of each configuration, because the generators don't have to be locked on a 50/60 Hz frequency with varying loads since the DC-frequency is 0 Hz. In a DC-grid the generators have a higher operating window, because they can run at different speeds. Especially when the power demand is not constant, a high profit can be made using this new configuration. [10, 33] On a DC-configuration most cables on-board of the ship are transporting DC and, therefore, don't have to deal with the reactive power using AC. The weight of the cables may, therefore, decrease depending on the power level.

On configurations using sodium borohydride as an energy carrier in combination with a fuel cell and battery even more important advantage arise, since the current from the fuel cell and to the battery is in DC. This means the configuration becomes less complex using a DC-grid. Less or lighter more efficient converters will be needed, thereby decreasing the total weight and increasing the efficiency of the system. An overview of a possible DC-configuration is shown in Figure 4.3.

Using a DC-grid on-board of vessel does have some technical challenges. There is, for example, not a sufficient standardised system because a DC-configurations is not very common. From safety perspective a DC-grid is also challenging because it doesn't have a zero-crossing like an AC has two times per period. Therefore, the DC has to be forced to zero to break the current [33]. Additional bigger and more complex systems will be needed on this configuration to secure the safety [52].

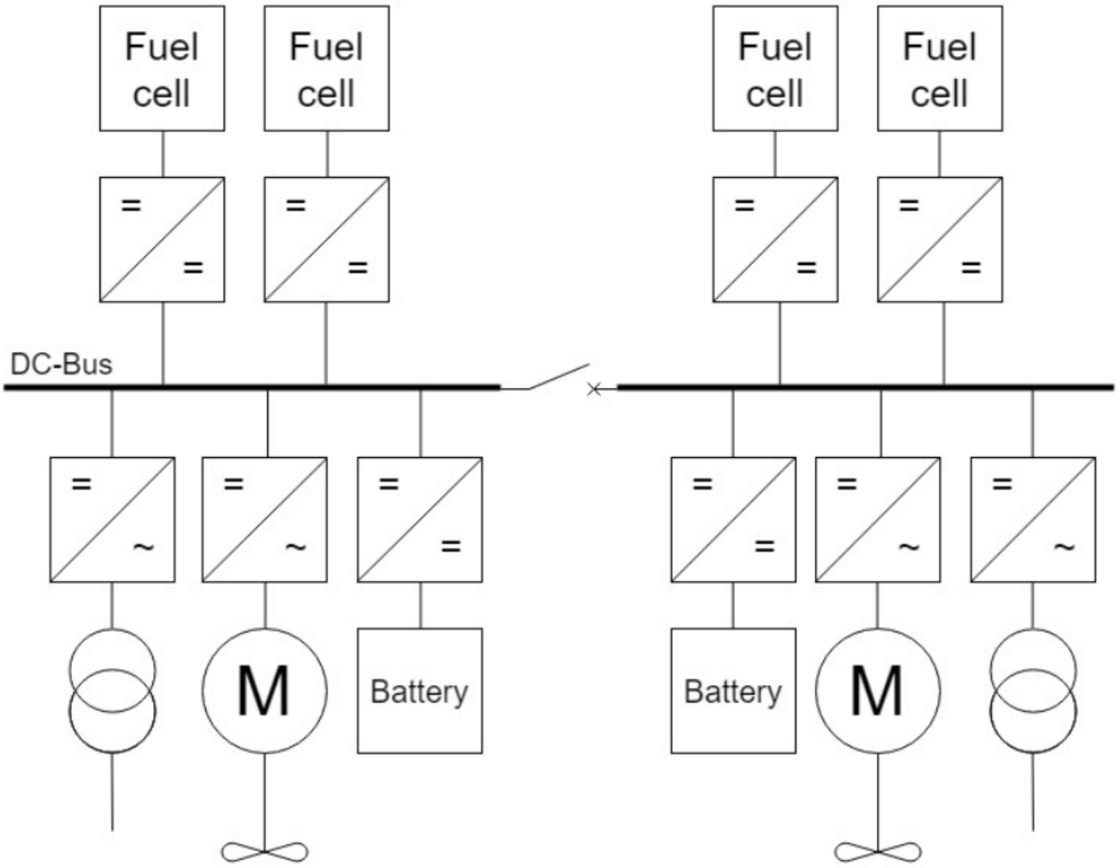

Figure 4.3: Possible DC-Configuration on fuel-cell powered vessel

4.2. Electric motors

From the DC-bus to the propulsion the electrical energy needs to be converted to mechanical energy. Electrical motors are capable to do so by creating an electromagnetic field to drive the rotor of the motor. An advantage of the electrical motor is that they produce less noise and vibrations compared to a ICE. This makes it a interesting choice for use on, for example, cruise vessels or submarines. Moreover, the manoeuvrability can be improved because the possibility to implement the motors in a podded propulsion. The most common types of electrical motors are shown in Figure 4.4 [63]. The most important types for the maritime industry will be discussed.

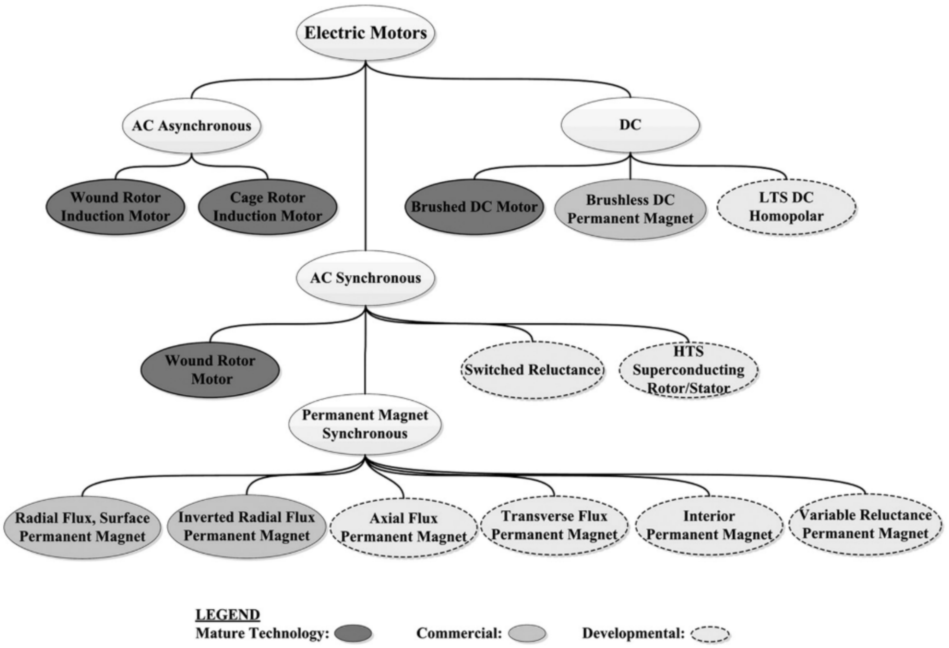

Figure 4.4: Electric motors by type and technology maturity [63]

In the past the most commonly used motor was de DC-motor. The main reason to select this motor is that the speed can be varied easily. The power, however, is limited to a maximum of 5 MW and maintenance becomes an issue when brushes are used in the motor. Since frequency converters can be used to control the speed of a AC-motor the DC-motor is just barely used on maritime applications [52].

The most commonly used electrical motors in maritime applications are the synchronous and the asynchronous AC motors. For AC motors a frequency converter is needed to operate at different speeds and to start the motor. The frequency of the AC-current determines the rotational speed of the motor. When a AC-bus is used on the vessel the sinus of the AC-current need to be converted to a continuous signal (DC) first. Thereafter, the required frequency is controlled by converting the DC-current back to an AC-current. The asynchronous motor is used for smaller application on-board of the ship [20].

There are many developments on the new types of electrical motors, such as: the permanent magnet motor, superconducting magnets and the high temperature superconducting motor. These newer types of motors have potential to improve efficiency, dynamic behaviour and power density. Especially the permanent magnet motors are already used on maritime applications. They are, however, still very complex and expensive. Looking at the current developments, many improvements and new applications can be expected [63].

4.3. Control systems

Since the system as a whole has many parameters from different sub-systems, which have to communicate with each other, a control system is needed to supply the power to the propulsion or other loads. A configuration of a system using hydrogen generation with sodium borohydride and a LT-PEMFC is researched and proposed by P.J.R. Pinto in 2013 for a stand-alone unit shown in Figure 4.5 [50]. In this research, also a batch reactor is used with a nickel foam supported ruthenium catalyst. Instead of a high pressure reactor a separate H_2 receiver is used and a LT-PEMFC converts the hydrogen to a DC current. A DC converter delivers the power to DC-bus, which is connected to the battery and the converters to the loads.

Looking at the control system in this configuration, most important controls are shown in the Figure 4.5. The pressure in the reactor is constantly measured and the flow to the reactor can be controlled. If a batch has delivered the right amount of hydrogen, for example when 98 % of the hydrogen is released, a new batch can be injected. The pressure in the reactor and to the receiver is controlled in the valve compressor combining the pressure measurement in the reactor and the H2-receiver. In the PEMFC, the temperature and the hydrogen- and airflow to the stack is controlled. At the DC-bus the load power is measured, which can be used to control the collaboration between battery, the load and hydrogen flow to the fuel cell.

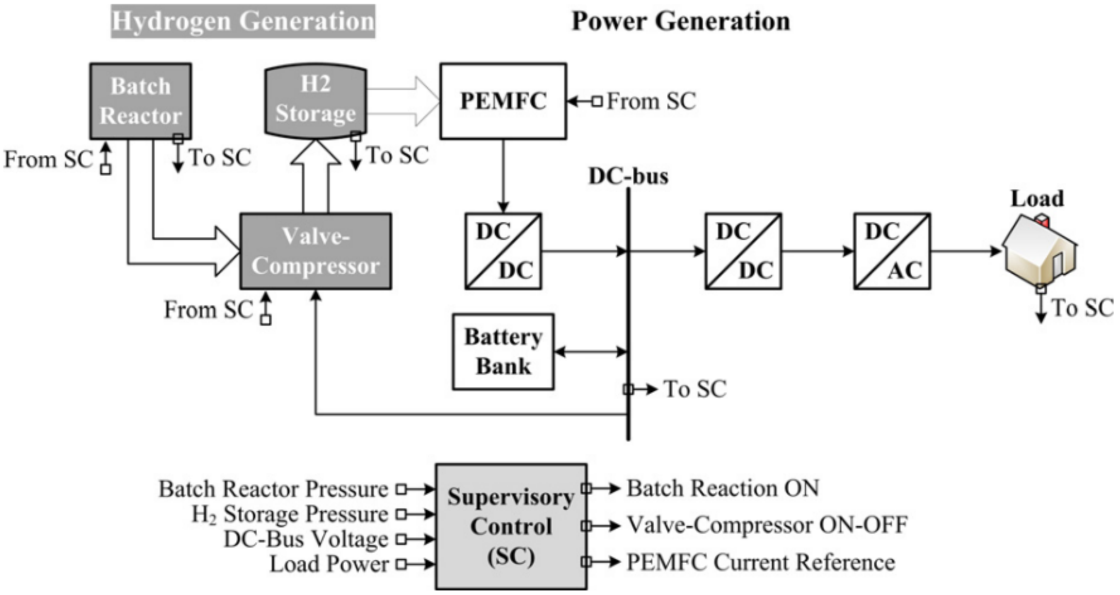

Fig. 1. Layout of the proposed stand-alone $NaBH_4$–PEMFC power system.

Figure 4.5: Lay-out of a $NaBH_4$ - PEMFC power management system [50]

A comparable configuration is used in this research. The control of the hydrogen flow will varies because it is done directly from the reactor and no, or just a small hydrogen receiver is needed. The batch reactor or a combination of batch reactors are used at higher pressures to buffer the hydrogen. At this stage of the research two fuel cell types are considered: the LT-PEMFC and the SOFC.

After the fuel cell, in most applications, there will be an extra DC/DC converter, because the voltage on the DC-BUS is often dependent on more loads than illustrated in Figure 4.5. A direct conversion to the voltage of the battery will in this case be impractical.

4.4. Battery systems

"A battery system is an electrochemical system that can store electric power with very high responsiveness" [18], but not as fast as a capacitor. Different from the fuel cell, the battery also stores the energy and not only converts the chemical energy to electrical energy. Moreover, the battery can also convert electrical energy to chemical energy. The specific energy is, however, much lower than for example a diesel system and batteries are, therefore, normally not used as main energy storage in most maritime applications. Battery systems are commonly used to: improve dynamic behaviour, increase fuel efficiency, peak-shaving or as an emergence device. Developments in batteries have led to higher energy densities and more reliable systems. Important parameters of the battery are the voltage, capacity and, for the dynamic behaviour, the battery response time. The response time of the battery depends on the electrochemical reaction taking place in the cell, which can be influenced by the material used in the anode and electrode. Most important parameters in the design choice of the type of battery system are: the density, reliability, safety, lifetime and cost.

Since the lithium-ion battery has been commercialised, it has become the most used battery in maritime applications [18]. A comparison between different types of batteries is made in Figure 4.6 [63]. The lithium-ion battery is one of the most compact solutions, which is highly available, in specific power and energy, like shown in this Ragone plot. Besides the batteries a super-capacitors or a combination of the two are used. Super-capacitors can deliver high amount of power in a short amount of time, making it a interesting solution when high peaks or a heavy fluctuating load is asked.

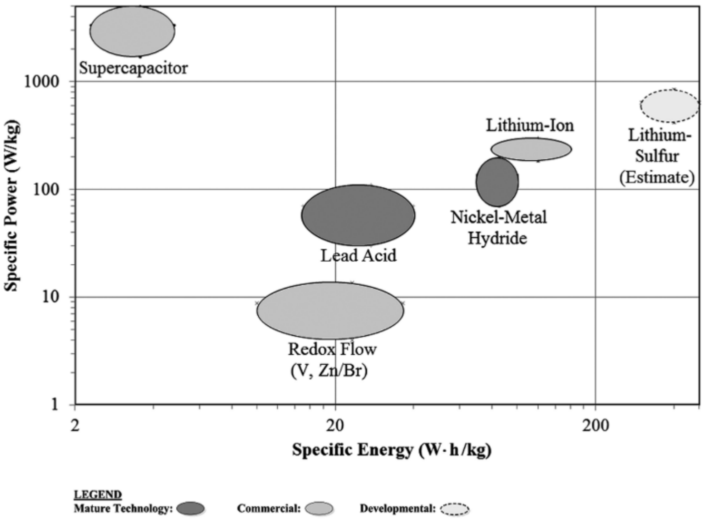

Figure 4.6: Specific energy and specific power comparison of energy storage technologies [63]

A battery-pack is needed to be able to deliver the right amount of power to the propulsion or other loads when a fuel cell is used on-board of a vessel, especially when a high performance dynamic behaviour is required. Depending on the type of fuel cell and the operational profile, the capacity of the battery and fuel cell can be optimised for cost, volume and weight.

Three modes are possible in the energy flow on a hybrid battery configuration. On the high power mode the battery delivers extra power to the load. On a low power mode the fuel cell delivers too much power to charge the battery. At standard mode the fuel cell can function on its own and no battery is needed. The different modes also need to be controlled in the power management system. An overview of the control system is given in Figure 4.7 [30].

An example of the relation between the fuel cell and the battery is shown in Figure 4.8 [13]. In this example tests have been done on a hybrid fuel cell-battery configuration on a tourist boat. The black line is the total power output to the propeller or the load on the propeller. To improve the dynamic behaviour of the system the fuel cell runs very continuously in comparison with the battery, as can be seen in the figure. The area under the total power-output is the amount of energy needed during the trip, or the energy which has to be converted from the fuel and battery. In this case the battery is not charged during the trip. The fuel cell is normally used to charge the battery at a lower load. The average power of the trip can be calculated and a design choice can be made to size the battery and fuel cell around this average when the load characteristics are known. The power delivered from the battery in relations to the power delivered from the fuel cell can be expressed in a degree of hybridisation (DOH), as shown in Equation 4.1 [1]. In case the peak power is high and the average power low, the battery delivers a high amount of power in an optimized configuration resulting in a high DOH. It is advisable to use a low DOH when the average power is high and peaks are relatively low.

$$DOH = \frac{\text{Battery power}}{\text{Battery power} + \text{Fuel cell power}} \tag{4.1}$$

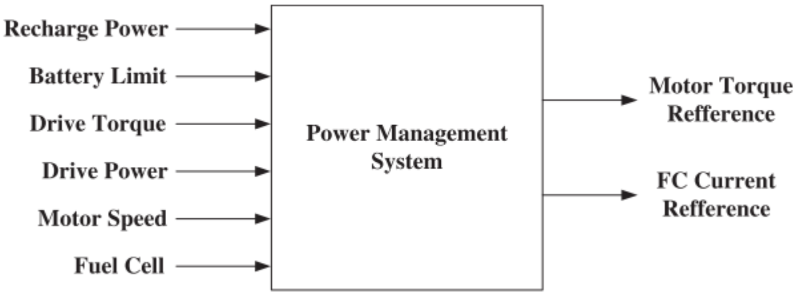

Figure 4.7: Battery power management system [30]

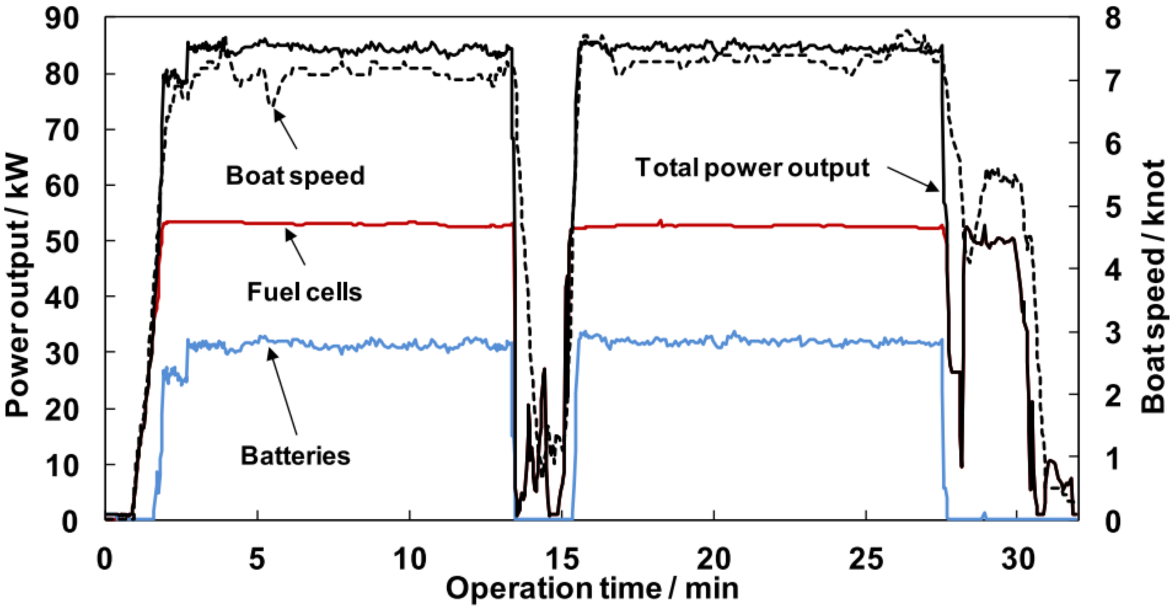

Figure 4.8: Power-output, boat speed, fuel cell power and battery power of a test operation on a tourist boat [13]

4.5. Component efficiencies

The transmission between the prime mover and the propeller are relativity small looking at the losses in the configuration. Efficiencies above 90 % are typical for the converters, used in a system like this. DC/DC-converters, for example, even reach efficiencies above 97% [37] on maritime applications. On ships, typical efficiencies of the research of I. Georgescu will be used: rectifier 98%, inverter 98%, transformer 100% [26].

The losses in the batteries are mainly caused while charging or discharging the battery. A lithium-ion battery-pack has a typical efficiency between 80 and 90 % [68]. Moreover, the power need to be converted to and from the battery causing some extra losses. From an efficiency point of view it is advisable to use the fuel cell as much as possible to prevent extra battery losses in the system. Fuel cells, however, also drop in efficiency at higher power demands. Thereby, the size and cost of the fuel cell will increase significantly when all power is installed in the fuel cell system.

Electric motors have been improved, looking at density and efficiency. An advantage in the maritime use of electric motors are even higher efficiencies, due to the big scale of implementation. Small scale electrical motors can reach efficiencies around 94%, like in the automotive industry [38]. Higher efficiencies till 98 % can be met at higher power demands like on the propulsion of the vessel.

4.6. Conclusion

A sodium borohydride system in combination with a fuel cell delivers a certain amount of power to the rest of the drive train. A DC-bus on-board of a vessel has some advantages for this system. Since the fuel cell and batteries are operating at DC, the conversion to and from the bus becomes more efficient. From safety perspective, however, some extra measures has to be taken to get control over the current in case of an emergency.

Normally, a battery system is needed besides the fuel cell. The battery is used for high load fluctuations and can be used for peak-shaving. A power management system needs to make sure the fuel cell and battery delivers the right amount of power to the loads. The size and type of the battery-system is depends on the operational profile of the vessel and the capability of the fuel cell to follow the load. Lithium-ion and lead acid batteries are the most used batteries in the maritime industry, because of its high power and energy density and its high availability. Super-capacitors can be considered for an even better dynamic behaviour.

A control system need to be implemented to match each subsystem of the drive train. Important measurements controlling the system are: the reactor pressure, the fuel cell reference current, the DC-bus voltage and the load power. Using these parameters, the power management of the each subsystem can be controlled.

5

Performance of configurations

The technical consequences, volumetric and gravimetric density is determined for each subsystem for different scenarios in the previous chapters. The results will now be combined to conclude the total system performance in weight and volume. First, the comparison in energy density of different type of fuels will be made and, hereafter, also the power density will be visualised in combination with the energy density in Ragone charts.

5.1. Energy density comparison

The energy is determined using the most compact configuration of Chapter 2. A comparison with other fuels is made in Figure 5.1 and 5.2 [69]. The most compact solution is a diesel configuration as can be concluded from these figures. The $NaBH4$-configuration is, however, a better options from sustainable point of view. The most compact scenario performs very well in volumetric density in comparison with LNG, and especially with the other hydrogen storage methods. Looking at the gravimetric energy density the system becomes very heavy during the trip. This is mainly caused by the fact that the hydrogen atoms in $NaBH_4$ are replaced by much heavier oxygen atoms in the spent-fuel. The vessel is much lighter when the fuel tank is just filled (start trip) in comparison with a full spent-fuel tank at the end of the trip. From these graphs, it can be concluded that the $NaBH_4$-system is competitive with the other fuels, especially when it's compared to other alternative clean fuels. On top of that, the $NaBH_4$-configuration is lighter and much more compact than compressed or liquid hydrogen storage.

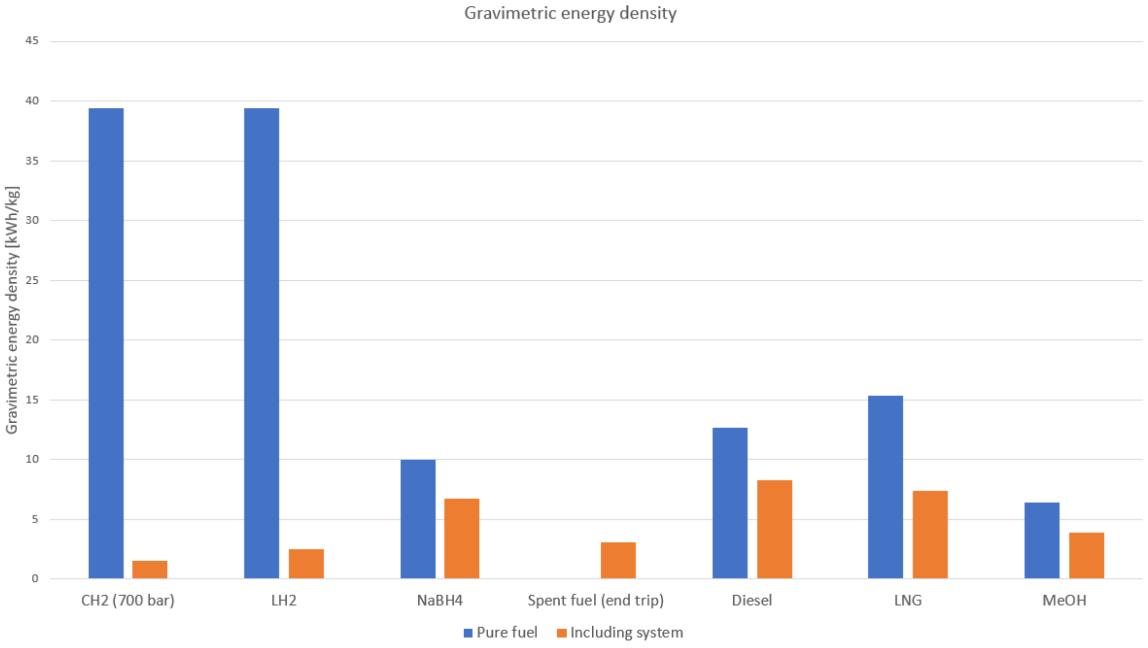

Figure 5.1: Comparison of different fuel types in gravimetric energy density, both as a pure fuel and including the fuel storage system [69]

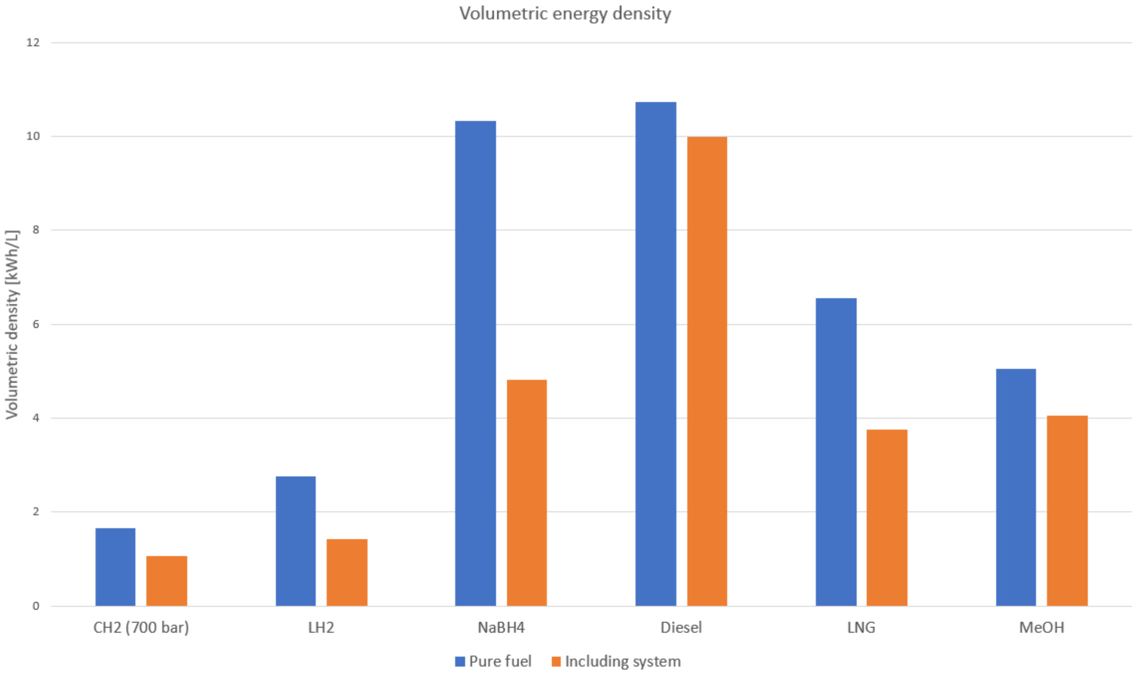

Figure 5.2: Comparison of different fuel types in volumetric energy density, both as a pure fuel and including the fuel storage system [69]

5.2. Ragone charts

The power density is calculated in Chapter 2. This is, however, not the complete power density of the system. Therefore, the fuel cell system is added to the weights and volumes. The results of the total power and energy density is presented in Table 5.1 and 5.2. The power density is known and all data can be combined in a Ragone chart, which provides an useful insight in the relation between power- and energy density. To determine this relation, the method of the research towards fuels cells in maritime applications is used [69].

In a Ragone plot the effective density of the system is visualised. In the effective density both power and energy density are related using a time-scale (t), like shown in Equation 5.1. The effective power density (P_{eff}) and the effective energy density (W_{eff}) are representing the densities of the whole system including the component dependent on both, the amount of power installed and the amount of energy on-board. The effective power density is calculated by making use of Equation 5.2, where P is the power density in Watt, t the operating time of the system in seconds and η the efficiency of the fuel cell. Combining both Equation 5.1 and 5.2 results in an expression for the effective energy density shown in Equation 5.3, where W represents the energy density in Watt hour.

$$\frac{W_{eff}}{P_{eff}} = t \tag{5.1}$$

$$P_{eff} = \frac{P}{1 + t\frac{P}{\eta W}} \tag{5.2}$$

$$W_{eff} = t \cdot P_{eff} = \frac{t \cdot P}{1 + t\frac{P}{\eta W}} \tag{5.3}$$

The power (P) is the sum of all systems dependent on the amount of power installed on the vessel, like the fuel cell, the reactor or an internal combustion engine in case of a diesel generator. The Energy density (W) represents the system volumes and weights dependent on the amount of energy stored on-board of the vessel, like the fuels and fuel-tanks. "It can be verified that these equations approach the limits $P_{eff} \approx P$ and $W_{eff} \approx \eta W$ for $t = 0$ and $t = \infty$ "[69].

The data combined results in the Ragone charts shown in Figure 5.3 [69]. In these charts the system operating time is shown in the straight black lines. The first line represents 1 hour operating time, the second 10 hours, the third 100 hours and the fourth 1000 hours. These lines are visualised to provide a clear overview in which case a system is more compact or lighter than another systems. The sodium borohydride configuration is compared for weight and volume to a diesel generator system, both a PEMFC and SOFC and a compressed hydrogen storage system.

A diesel generator system is compared to the $NaBH_4$-configurations in the first two plots of Figure 5.3. In cyan the most compact configuration, described in Chapter 2, in combination with a PEMFC is illustrated. The range of this scenario is given by the maximum and minimum densities. The volumetric power density is slightly higher than the density of a diesel generator. Developments in the size of the reactor will, however, improve the power density in the future. The graphs show a crossing point around 20 operating hours for the maximum volumetric densities. After this point the diesel system becomes more compact. Until 100 hours, however, the difference between the two systems are still very small. The difference between the minimum densities is higher, because a wide range for the reactor is chosen.

In second two graphs of Figure 5.3 two types of fuel cells are compared for both scenarios. It will be useful to know if there's a point where it becomes more attractive to implement an SOFC system because of the higher efficiency of an SOFC system. Looking at the maximum densities of scenario 2 this point is both present in gravimetric and volumetric density graphs. After 1000 hours is can be expected that a SOFC system becomes more compact than an PEMFC system. For long trips this would be an interesting case to consider in the design of the drive train.

In the third pair of graphs of Figure 5.3 the SB-system is compared to a compressed hydrogen system at 700 bar. In these graphs it can be clearly seen that the power density of the fuel cells in the compressed hydrogen system is very high. This, because only a very light and compact fuel cell module is needed. The fuel and fuel-tanks, however, are very large and heavy. Therefore, already between 10 and 50 hours, the complete system becomes much larger than other systems. Between 40 and 300 hours the compressed hydrogen system becomes much heavier. This results in the fact that, from volumetric and gravimetric perspective, the compressed hydrogen systems are only interesting for short trips.

Figure 5.3 is an estimation of different fuels system defined by some boundary conditions. Several volumes and weights are not taken into account in this comparison. The exhaust pipes for the diesel system are, for example, not included because its highly dependent on the design of the vessel. The size of this system can, however, decrease the power density significant. Systems like batteries, scrubbers and waste heat heat recovery systems are not included for the same reason.

A useful starting point for a conceptual design can be made from these results. The next step is to decide which impact the system has on safety, cost and the environment. A diesel generator is in many cases the most compact and safe solution, because of the maturity of the technology and the high energy density of the fuel. However, from environmental perspective it is the worst solution.

Table 5.1: Gravimetric and volumetric energy density of diesel, compressed hydrogen at 700 bar [69] and SB, including the system

	Gravimetric Density (Wh/kg)	Volumetric Density (Wh/L)
Diesel	8300	8200
Scenario 1	1010-1200	860-1300
Scenario 2	2800-3200	3620-5100
CH_2	2162	1066

Table 5.2: Gravimetric and volumetric power density of a diesel system [69] and sodium borohydride system (including two types of fuel cells)

	Gravimetric Density (W/kg)	Volumetric Density (W/L)	HHV Efficiency (%)
Diesel genset	45-72	32-50	34-44
SB-system 1 (PEMFC)	10-61	11-63	33-50
SB-system 2 (PEMFC)	10-60	11-61	34-49
SB-system 1 (SOFC)	5-38	3-22	38-55
SB-system 2 (SOFC)	5-37	3-22	37-54
PEMFC (CH_2)	250-1000	300-1550	34-50

5.3. Conclusion

All sub-systems added together result in a total overview of the drive train. From this overview gravimetric and volumetric energy and power density is derived. The combination of this results in Ragone charts are even more relevant for the system volume and weight. The most compact solution, in terms of energy density, is heavy compared to fuels like diesel, LNG and methanol. Especially in the end of the trip when all spent-fuel is produced, the weight of the vessel increases. In comparison with liquid or compressed hydrogen the total system gravimetric energy density performs slightly better.

Looking at the volume of the system, the concept of the dry fuel and filtered spent-fuel performs very well compared to other alternative fuels, such as methanol, LNG and compressed or liquid hydrogen. A general diesel system is, however, much more compact. This, mainly because of the fact that the spent-fuel need to be stored on-board of the vessel and the tank-systems are estimated larger and heavier than, for example, an integrated diesel tank.

The energy density is not the only parameter which determines the size and weight of the whole system. The power density of the system need to be added up to the energy density in order to determine the total size and weight. This is, however, different for each type of application and, therefore, these two are combined in Ragone charts. From these plots some important conclusions can be drawn. In the most compact case of a $NaBH_4$-configuration, the volume of the system is comparable with a diesel system. The system can even be more compact until trips around 10 operating hours. Until 200 hours, the system volume is still close to the volume of a diesel system. Hereafter, the difference becomes more significant.

There is a point where the SOFC-system becomes more compact or lighter than a PEMFC-system because of the SOFC has a higher efficiency. For the gravimetric density this point lies around 250 operating hours, and for the volume around 1000 operating hours, using the optimum densities. Therefore, from system density point of view, the SOFC becomes interesting to consider for long trips.

It can be concluded that the power density of the compressed hydrogen system is much higher compared to a $NaBH_4$-system. The fuel has, however, a much lower energy density, especially looking at the volume. The $NaBH_4$-system becomes more compact between 10 and 50 operating hours.

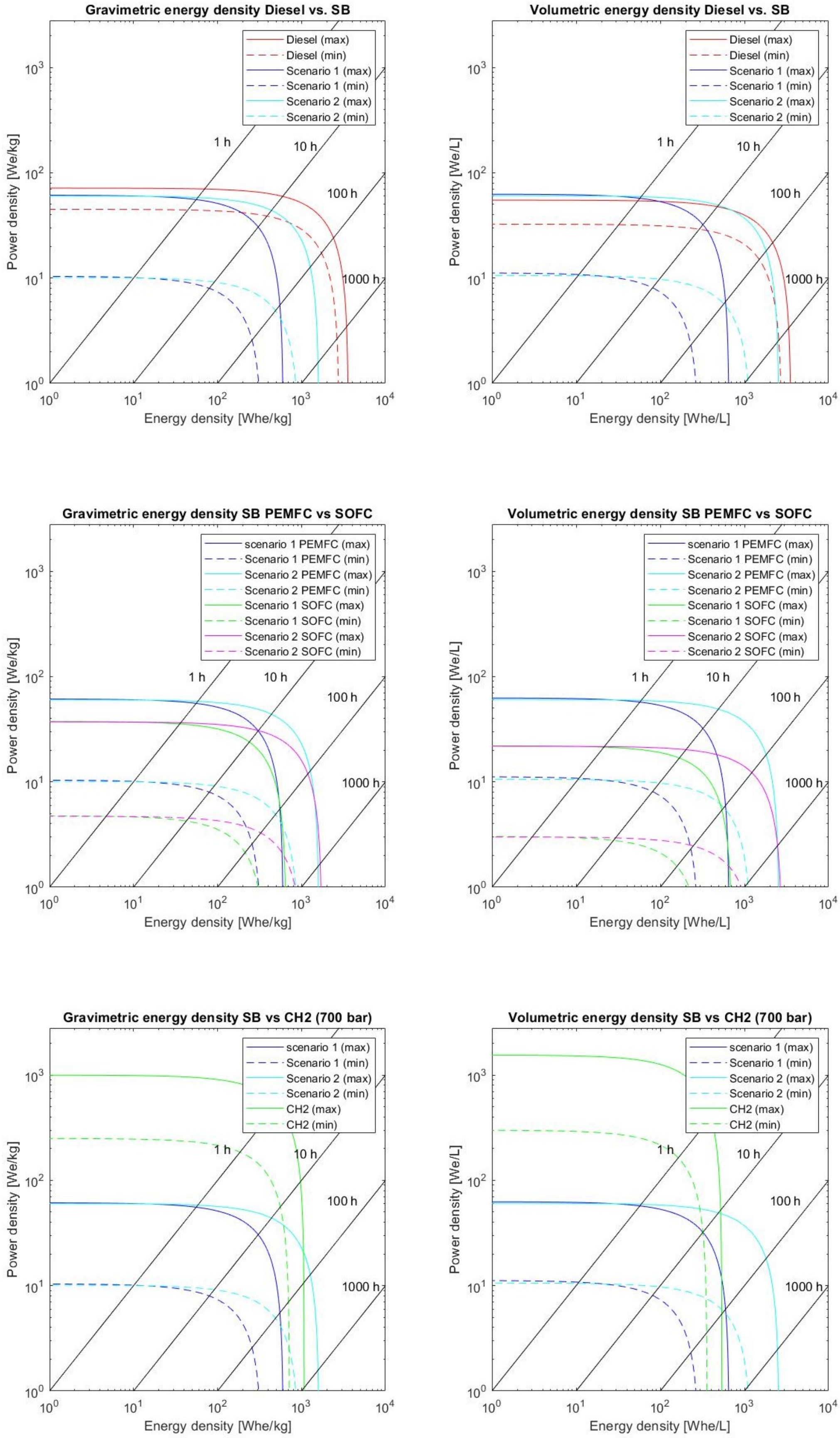

Figure 5.3: Visualisation of the energy and power density in Ragone plots [69]

6

Safety and regulations

Implementing a system using sodium borohydride to release hydrogen on-board of a ship, needs a detailed study on safety and potential hazards for practical use on the vessel. A risk analysis has to be made based on the potential hazards because the fuels and systems have never been classified for maritime use before and.

First, a description of the fuels is given. Based on material safety data sheets (MSDS) and chemical cards of the fuels, or comparable fuels, the potential hazards are concluded. Besides the fuel description comparable regulation is studied to give an insight in the possible outcomes and opportunities when the system is reviewed by classification, the flag-state or other involved parties.

6.1. Sodium borohydride solutions

A sodium borohydride solution consist of $NaBH_4$, H_2O and, in this case, $NaOH$. The sodium hydroxide is added to this solution to make the fuel more stable. Small particles of solid sodium borohydride can be found in the solution at high concentrations of $NaBH_4$, because not everything can be solved in this composition. At higher temperatures or pressures, like in the mix chamber, more or all solid sodium borohydride are dissolved in the water.

The solutions proposed in this research are not included in the International Chemical Safety Cards (ICSC) database. The aqueous solution in different ratios (max. 12 wt.% $NaBH_4$ and max. 40 wt.% NaOH) and the dry sodium borohydride powder are, however, known with United Nations (UN) numbers 3320 and 1426, as is also shown in Appendix E: Chemical cards. Until the MSDS of these solutions is made, the MSDS of these solution and dry powder is used for the safety analysis. As can be seen in the fuel ratios of, for example, Fuel 30, 50 and 66, the solution contains way more $NaBH_4$ and less NaOH than the UN 3320.

The sodium borohydride solution (UN. 3320) belongs to: the strong bases, metal hydrides, metal alkyls, silanes and the water and aqueous solutions. The alkalinity of the solution depends on the ratios $NaOH$ and $NaBH_4$. More sodium hydroxide leads to a higher pH-value, a more stable solution and, therefore, a longer half-life. The pH-value of Fuel 50, used for the configuration with an acid accelerator, the pH is between 10-14 or, more precisely, around pH 13 for a half-life of 240 days.

The solution is a strong base and is, therefore, labelled as corrosive. Not all materials can be used to store the fuel and ingestion, skin and eye contact needs to be prevented like stated on the chemical cards. The solution itself is non-flammable. The hydrogen released from the fuel, however, needs to be taken into account because of its high flammability and explosion hazard. Sodium borohydride already reacts with the water in the solution and, therefore, a stabiliser is added to make the solution more stable. The half-life of Fuel 50 with 7.5 wt.% sodium hydroxide is 240 days. After 240 days half of the fuel reacted and thus hydrogen is released in tank. To approach the amount of hydrogen released, Equation 6.1 is used for this first-order reaction:

$$N(t) = N_0 \left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}} \tag{6.1}$$

With N as the amount of moles hydrogen generated on a specific moment in time, N_0 the initial condition, t the time and $t_{1/2}$ the half-life of the reaction in the tank. From this equation it can be concluded that the amount of hydrogen generated reduces over time. In Figure 6.1 an example of the amount of hydrogen generated in the tank is shown for 1 kilogram of Fuel 50. As can be seen here, after 240 days half of the hydrogen gas in the solution is released. This means that on the first day more hydrogen is generated than on the other days. The amount of hydrogen generated on the first day is around 0.3 grams per kilogram of Fuel 50. The amount of hydrogen generated in the tank is relatively small, which makes it easier to ventilate and stay within a safe region. More addition of sodium hydroxide results in a more stable fuel and this can be a (design)choice when the hydrogen release is still to high.

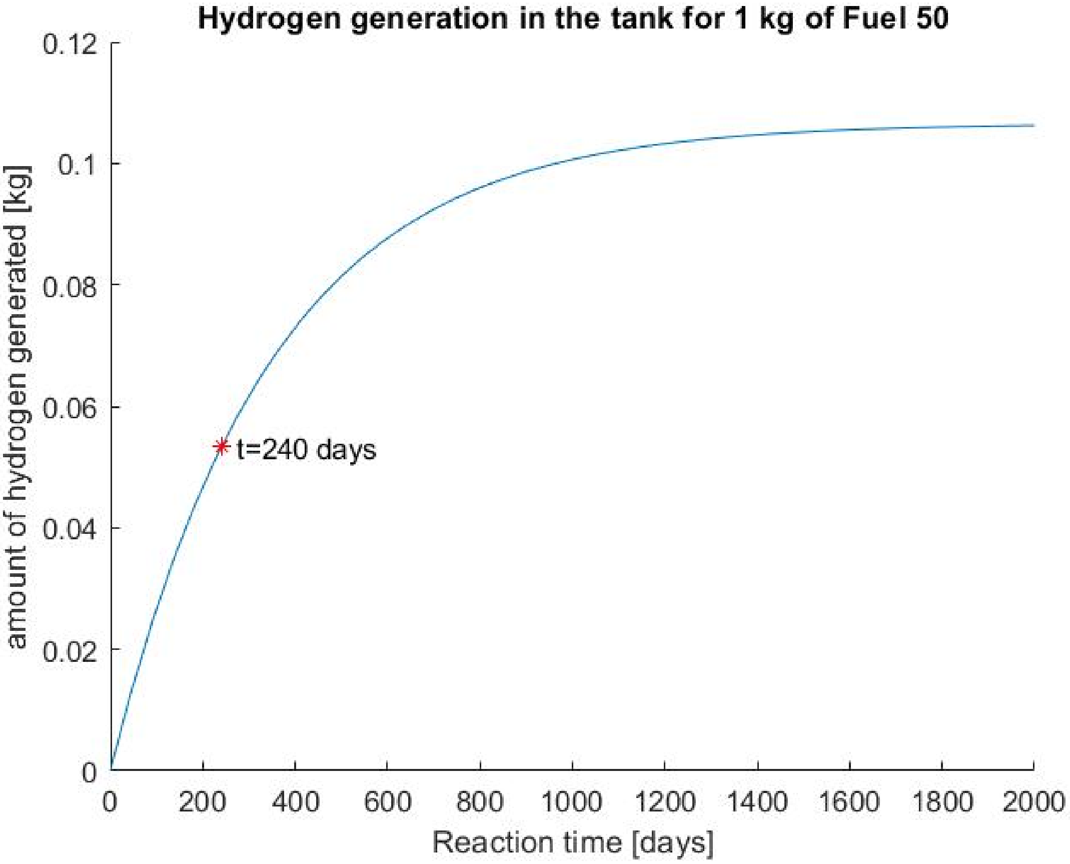

Figure 6.1: Hydrogen generation in a Fuel 50 tank for 1 kg of fuel

6.2. Hydrochloric acid

Hydrochloric acid (UN 1789) can be used to accelerate the reaction in the mix chamber. The reaction time in the batch reactor is reduced to 3 minutes to release 98% of the hydrogen from the reaction of sodium borohydride with ultra-pure water using a aqueous hydrochloric acid solution of 30 wt.% HCL . This hydrochloric acid solution is also abbreviated as A30 (HCL-Activator, 30 wt.%) in this report.

The chemical card are shown in Appendix E. As is shown here, the hydrochloric acid is known as a highly corrosive solution with a pH smaller than 1. This liquid is classified as a dangerous liquid and it is, therefore, of high importance to meet the precautionary statements. Especially contact with skin, eyes, inhalation and ingestion needs to be excluded.

The tanks/bags containing the hydrochloric acid must be provided with a coating or material, which resist the highly acidic solution. Any leakage can cause damage on the construction of the ship because most metals can't resist such acidic solutions. This means contact with the acid must be avoided and human handling need to be minimized or done under highly safe conditions.

The acid is non-flammable and non-explosive, so there are no fire and explosion hazards for the activator on its own. A reaction with other materials, however, can cause fire or explosion hazards. Contact with the Fuel 50 must be avoided, because the acid will accelerate the release of hydrogen rapidly. Only in the mix chamber this reaction will take place in a controlled environment. Hydrochloric acid and Fuel 50 may never come in contact with each other outside the mix chamber and, therefore, the tanks must be separated adequately.

The hydrochloric acid can be stored at atmospheric conditions. Only a few metals are suitable for direct contact with the hydrochloric acid. Metals like tantalum and Hastelloy B and C are known in the industry to be resistance to the hydrochloric acid. Rubber lining steel, a protection of multiple rubber layers, would be another method to protect the tank.

The piping systems around the tank are normally equipped with a lining of fluoropolymer or polypropylene for the liquid acid. For the vapours, also fiberglass reinforced plastics are used.

Ventilation systems and scrubbers needs to be installed in the tank to absorb any vapour from the hydrochloric acid. A pressure- and vacuum-valve needs to be present in the tank to prevent over- or underpressure. Moreover, an overflow line on the tank is needed to make sure the tank does not exceeds its maximum level. Finally, chemical hoses designed specifically for hydrochloric acid must be used for loading this activator [12].

6.3. Hydrogen

Hydrogen is the most dangerous material present in this system looking at fire and explosion hazards. The amount of hydrogen gas, however, is minimised because of the storage in a stabilized solution or dry powder. It is still important to determine adequately where the hydrogen gas can appear. In this system most of the hydrogen will be handled in the mix-chamber, the fuel cell and in between these two systems. A smaller amount of hydrogen can be found in the fuel and spent-fuel, like mentioned in the previous subsection. Possible hazards and other safety concerning information can be found in Appendix E.

Hydrogen is known for its extremely high flammability. Therefore, each room containing any hydrogen gas requires adequate ventilation and temperature control. As is reported on the chemical card, prevention of fire and explosions can be met by avoiding open flames, sparks and smoking. The hydrogen needs to be handled in a closed ventilated system. Moreover, electrical equipment and lighting needs to be explosion-proof and only sparking free hand-tools can be used.

Hydrogen itself is an odourless colourless gas and it is hard to detect for the human senses. In each room containing hydrogen systems, sufficient detection need to be placed. Especially places where hydrogen accumulates needs special attention. Hydrogen is lighter than air, so the most dangerous places will be around the ceilings of the room. Since normal flammable gas detectors are not suitable to measure the concentration of hydrogen, the right detectors need to be chosen with care.

Leakage of hydrogen is harder to prevent than other fuels like diesel and diesel gases, because hydrogen is a very small molecule. Therefore, all piping and storage systems must be provided with the right materials. Standards for pipeline systems can be found in the American Society of Mechanical Engineers (ASME) B31.12 reports and the European Industrial Gasses Association and Industrial Gases Council documents (EIGA IGC Doc 100/03/E & 121/04/E) [5, 7]. The operating temperature, pressure, hydrogen embrittlement and corrosion needs to be taken into account when a hydrogen piping system is designed. The ASME B31 regulations can be used as guideline to determine material type, thickness, anti-corrosion coatings etc..

Its preferable to place systems containing hydrogen in the open air or close to open air. The chance on fire or explosion hazards can be minimized in open air because hydrogen gas evaporates very quickly. Therefore, its preferable to place the mix-chamber and fuel cell on deck, where the hydrogen gas can be released in the environment quickly.

As is shown in the MSDS of hydrogen, the health hazard is very small in comparison with the explosion hazard. It still has to be taken into account that high concentrations can cause an oxygen-deficient environment [65].

6.4. Spent-fuel

After the mix-chamber the hydrogen is separated from the residual materials, the spent-fuel. This product can be stored in a separate tank or volume-exchange tank. The content of the spent-fuel is dependent on multiple parameters like: the temperature, pressure, type of activator, fuel contents and type of reactor. In most researches it is assumed a aqueous solution of sodium metaborate $NaBO_2$ in water is produced, but also $Na_2B_4O_7$ (Borax) and other variants are formed. Most of the sodium hydroxide is preserved like tested by H2Fuel systems.

The spent-fuel can be described as a aqueous solution containing $Na_2B_4O_7$ and $NaOH$. Small solids ‘float’ through the liquid because not all the materials are dissolved. The borax and sodium hydroxide make the solution basic and tests resulted in a pH-value between 5 and 10. The solution itself has a pH-value of 7.2

[64].

The reaction is completed for 98% in the mix chamber. This means a small amount of hydrogen is still released from the moment the spent-fuel leaves the mix chamber. This also means the spent-fuel tank needs to be ventilated to prevent accumulation of hydrogen in the tank. Calculated from the reaction this will be less than 1 gram per liter spent-fuel.

Looking at the MSDS of a borax solution only hazards can be found in health issues. Contact with eyes, skin, ingestion and inhalation needs to be avoided. Using a Borax solution will not lead to any fire or explosion hazards, since the solution is not flammable. The residual hydrogen in the spent-fuel, however, needs to be taken into account in the fire or explosion hazards.

6.5. Regulations

Specific regulations for these type of configurations in the maritime industry does not exist yet, because a sodium borohydride system has never been implemented for commercial use on a vessel. Therefore, this system cannot be classified within the current regulations. A risk-analysis needs to be made first to quantify the possible hazards within this system. Depending on the outcome of the risk-analysis, new regulations can be made to make a safe implementation of the system possible. New regulations needs to be approved by the class society and the flag state.

Although the regulations for this system do not exist yet, comparable regulations can be consulted to use for the risk-analysis. Parties and codes like: the International Maritime Organisation (IMO), Safety Of Life At Sea (SOLAS), Centrale Commissie voor de Rijnvaart (inland shipping) (CCR), International code of safety for ships using Gases or other low-flashpoint Fuels (IGF-code), International Bulk Chemical code (IBC), the International Maritime Dangerous Goods code (IMDG-code), the flag state and the classification societies are relevant within this project. A 'pre-study' is done towards some of these codes. The most important or relevant regulations will be highlighted in this section.

6.5.1. IGF-Code

The IGF-code is especially relevant for the parts in the system where hydrogen gas is processed. Chapter 2.3 till 4.3 describe the most important requirements using a low flashpoint fuel on-board of a vessel. In general the functional requirements for low-flashpoint fuels can be found in chapter 3.2 of the IGF-code. To ensure a safe system a risk assessment needs to be made according the following rules:

> *4.2.1 A risk assessment shall be conducted to ensure that risks arising from the use of low-flashpoint fuels affecting persons on board, the environment, the structural strength or the integrity of the ship are addressed. Consideration shall be given to the hazards associated with physical layout, operation and maintenance, following any reasonably foreseeable failure.*
>
> *4.2.2 For ships to which part A-1 applies, the risk assessment required by 4.2.1 need only be conducted where explicitly required by paragraphs 5.10.5, 5.12.3, 6.4.1.1, 6.4.15.4.7.2, 8.3.1.1, 13.4.1, 13.7 and 15.8.1.10 as well as by paragraphs 4.4 and 6.8 of the annex.*
>
> *4.2.3 The risks shall be analysed using acceptable and recognized risk analysis techniques, and loss of function, component damage, fire, explosion and electric shock shall as a minimum be considered. The analysis shall ensure that risks are eliminated wherever possible. Risks which cannot be eliminated shall be mitigated as necessary. Details of risks, and the means by which they are mitigated, shall be documented to the satisfaction of the Administration.*

Hereafter, most of the regulations in this code are based on liquid natural gas fuelled ships, but will probably be comparable to the future hydrogen gas regulations. The regulations for fuel tanks are, however, not very representative for the tanks on-board of a vessel, because the fuels are not mentioned in the regulations and are no low-flashpoint fuels. For the machinery space, from chapter 5.4, the regulation will be comparable for the mix chamber and fuel cell. Some examples of these regulations are:

5.5.1 A single failure within the fuel system shall not lead to a gas release into the machinery space.

5.5.2 All fuel piping within machinery space boundaries shall be enclosed in a gas tight enclosure in accordance with 9.6.

5.6.2 Measures shall be applied to protect against explosion, damage of areas outside of the machinery space and ensure redundancy of power supply. The following arrangement shall be provided but may not be limited to:
.1 gas detector;
.2 shutoff valve;
.3 redundancy; and
.4 efficient ventilation.

5.6.4 Distribution of engines between the different machinery spaces shall be such that shutdown of fuel supply to any one machinery space does not lead to an unacceptable loss of power.

5.7.2 Fuel piping shall not be led directly through accommodation spaces, service spaces, electrical equipment rooms or control stations as defined in the SOLAS Convention.

5.8 Fuel preparation rooms shall be located on an open deck, unless those rooms are arranged and fitted in accordance with the regulations of this Code for tank connection spaces.

5.10.1 Drip trays shall be fitted where leakage may occur which can cause damage to the ship structure or where limitation of the area which is effected from a spill is necessary.

Note: These regulations are for ships using liquid natural gas fuel only.

In this part of the code a useful insight is provided on how the systems on-board of a vessel can be implemented. First of all, it is advisable to place systems like the mix chamber and fuel cell on-deck, close to open air. Extra redundancy can be met when the mix chamber is placed separately from the fuel cell, for example, in two separate rooms in the deck-house. Shut-off valves between these two systems can reduce damage and hazards in case of a failure and sufficient ventilation and detection is of very high importance. Not mentioned above is the B/5-rule described a few times in the code. Often machinery and fuel tanks needs to be placed within 1/5 of the beam of the vessel, measured from the summer load line. This rule is based on the damage at a collision. This means the fuel cell and mix chamber can, most probably, not be placed on the sides of the vessel. There is a chance that the fuel tanks has to fulfil the ‘B/5-rule’.

6.5.2. IBC-code

The IBC-code is a code for chemical carriers[31]. Fuels, or comparable fuels, like a high concentrated sodium borohydride solution and hydrochloric acid are, however, more known on this type of vessel. Therefore, lessons can be learned for the design and safety assessment for the implementation on other types of vessels. A list of materials is included in this code and comparable fuels are summed up in Table 6.1 [31]. Some of the important data are explained next. A type 3 ship (column c) is defined as:

2.1.2.3 A type 3 ship is a chemical tanker intended to transport chapter 17 products with sufficiently severe environmental and safety hazards which require a moderate degree of containment to increase survival capability in a damaged condition.

In column d the tank type is specified as follows: 1=independent tank 2=integral tank G=gravity tank and P = pressurized tank. Hydrochloric acid has to be stored in a independent gravity tank on a chemical carrier and more stable sodium borohydride solutions can be stored in a integral gravity tank. This does not conclude hydrochloric acid can’t be stored in the integral tank or bags on other types of vessels, but it is a possible scenario. Both tanks need controlled ventilation. The sodium borohydride solution of less than 15% needs also ventilation for environmental control or gas padding can be applied, ‘by filling the cargo tank and associated piping systems with a gas which separates the cargo from the air, and maintaining that condition’ (9.1.3.2). Advantage of padding is that the fuel stays clean from pollution of the outside air and, therefore, a more efficient reaction takes place in the mix chamber. Hydrochloric acid does not need environmental control on chemical carriers. For both HCL and the SB <15 wt.% solutions restricted gauging needs to be implemented as described below:

> *13.1.2 Restricted device - which penetrates the tank and which, when in use, permits a small quantity of cargo vapour or liquid to be exposed to the atmosphere. When not in use, the device is completely closed. The design should ensure that no dangerous escape of tank contents (liquid or spray) can take place in opening the device.*

No fire protection is needed for both fuels, but since Fuel 50 is less stable than the solution mentioned in the table this should be reconsidered in the risk assessment and design phase of the project. At last; Chapter 15.11 does mention more special requirements storing acids on a chemical tanker.

6.5.3. IMDG-Code

In the International Maritime Dangerous Goods (IMDG) code [32], regulations can be found for the transportation for goods or comparable goods used in this system. An overview is made of the important and comparable UN numbers in this system in Table 6.2 [32]. Only the hydrochloric acid is the exact solution, which is also used for the system. The other substances are comparable to $NaBH_4$-solutions, but with another weight percentage. The sodium borohydride – sodium hydroxide solution, for example, has no more 12% sodium borohydride by mass.

The materials can be transported in limited quantities depending on the type of package. A IBC-container can, for example, be used for some of the products when the right instructions are met. Moreover, portable tanks, like transported on a truck, are mentioned here. Packages in limited quantities have to be stored on-deck.

6.6. Conclusion

It can be concluded that the use of hydrochloric acid is a big challenge from safety perspective. Therefore, the options to use a catalyst instead of an acid is highly recommended for the future use of these systems. Research towards this accelerator is already planned and might make the system more realistic to implement on vessels. Other hazards are fire and explosion hazards, from the hydrogen released by the fuels, in the mix chamber and in the fuel cell. Sufficient detection, protection and prevention need to be taken into account to secure the safety on-board.

Table 6.1: Overview of comparable fuels regulation in the IBC-code [31]

a	b	c	d	e	f	I -Electrical equipement	h	i	j	k	l	m		
Product name	UN no.	Ship type	Tank type	Tank Vents.	T. Env. Cont.	I' Class	I" Group	I"' Flashpoint >60 C	gauging	Vapor Det.	Fire Prot.	Material	Resp& Eye	Special Requirements
Hydrochloric acid	1789	3	IG	Cont	No		NF		R	T	No		E(f)	15.11
Sodium borohydride (15% or less) /Sodium hydroxide solution		3	2G	Cont	Vent or Pad (gas)	NF		R	T	No		No	15.16.1	
Sodium hydroide solution	1824	3	2G	open	No		NF		Open	No	No	N8	No	

Table 6.2: Overview of comparable fuels regulation in the IMDG-code [32].

UN No.	Proper shipping name (PSN)	Class or division	Subsidiairy risk(s)	Packing group	Special provisions	Limited quantity	Excepted quantities	Packing Instructions	Provision	IBC instructions	IBC provision	Tank instructions	Tank provisions	EmS	Stowage and handling	Segregation	Properties and observations
1049	HYDROGEN, COMPRESSED	2.2	-	-	-	0	E0	P200	PP91	-	-	-	-	F-D, S-U	Category E SW2	SG46	Flammable, odourless gas, Explosive limits: 4% to 75%. Much lighter than air (0.07) Crystalline powder. In contact
1426	SODIUM BOROHYDRIDE	4.3	-	I	-	0	E0	P403	PP31	-	-	-	-	F-G, S-O	Category E H1	SG26 SG35	with water, acids or moisture, evolves hydrogen, which may be ignited by the heat of the reaction Colourless liquid. An aqueous
1789	Hydrochloric Acid (1)	8	-	II	-	1 L	E2	P001	-	IBC02	B20	T8	TP2	F-A, S-B	Category C	-	solution of the gas hydrogen chloride. Highly corrosive to most metals. Causes burns to skin, eyes and mucous membranes.
1789	Hydrochloric acid (2)	8	-	III	223	5 L	E1	P001 LP01	-	IBC03	-	T4	TP1	F-A, S-B	Category C	-	See entry above
3182	Metal hydrides, Flammable N.O.S.	4.1	-	II	274	1 kg	E2	P410	PP31, PP40	IBC04	-	T3	TP33	F-A, S-G	Category E	-	-
3182	Metal hydrides, Flammable N.O.S.	4.1	-	III	223 274	5 kg	E1	P002	PP31	IBC04	-	T1	TP33	F-A, S-G	Category E	-	-
3320	SODIUM BOROHYDRIDE AND SODIUM HYDROXIDE SOLUTION with not more than 12% sodium borohydride and not more than 40% sodium hydroxide, by mass	8	-	II	-	1 L	E2	P001	-	IBC02	-	T7	TP2	F-A, S-B	Category A	SG35	Off-white clear liquid with a slight hydrocarbon odour. Reacts violently with acids. In contact with acids or if diluted with large amount of water, evolves hydrogen gas and heat. Causes burns to skin, eyes and mucous membranes
3320	SODIUM BOROHYDRIDE AND SODIUM HYDROXIDE SOLUTION with not more than 12% sodium borohydride and not more than 40% sodium hydroxide, by mass	8	-	III	223	5 L	E1	P001 LP01	-	IBC03	-	T4	TP2	F-A, S-B	Category A	SG35	See entry above

II

Modelling and simulation

7

Method and simulation description

In the first part of this research a study to the volumes and weights of a sodium borohydride system has been done. This part resulted in some compact configurations, which are competitive to with other sustainable fuels. All components of this system are technical feasible for implementation on-board of vessel. It is, however, still unknown how this system behaves in operating condition.

Part two of this report studies the dynamic behaviour of a sodium borohydride application. For now focus is put on a single specific case. Both long term and short term dynamic behaviour on the Clipper the Stad Amsterdam (CSA) are measured. A possible drive train is modelled to predict its performance on load fluctuations from the required hotel load of the vessel. The method used to build the model and each subsystem of the model will be described in this chapter.

7.1. Method

The modelling process is illustrated in Figure 7.1 where the different steps of the approach are schematised. Each step will be explained in more detail in this section.

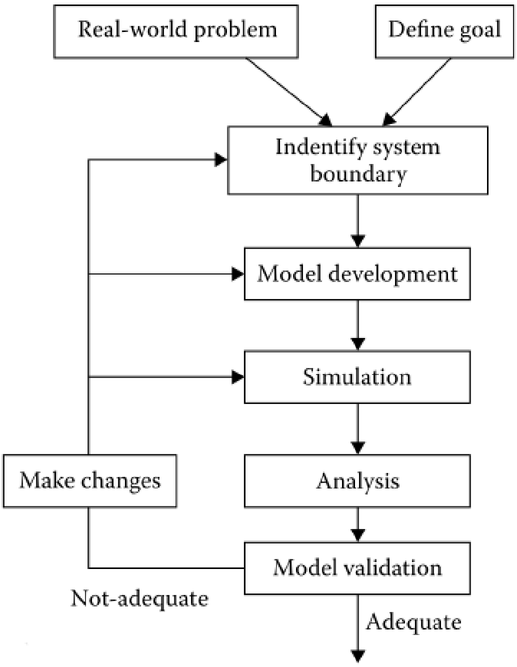

Figure 7.1: Abstract follow-up three of a modelling process [70]

7.1.1. Define goal

The overall goal of this model is to find the performance under a variable load of the CSA. The simulation is built to analyse whether the system is capable supply the adequate power to its users. Different methods and iteration steps are made to find a fitted solution for the CSA.

7.1.2. Real-world problem

A feasibility study is performed for the implementation of a sodium borohydride system on-board of the CSA, also described in Chapter 8. Whether this application can supply its power fast enough is till this point unknown. It should be capable of handling on-board fluctuation in power demand. In an attempt to gather important real-world model input, on-board measurements have been conducted. The gathered data is used for simulation construction and testing. Parameters like the short-term hotel load and long-term load need to be known as a starting point of the model and the input variables are determined in this part of the process. For all subsystems input parameters are needed to obtain a realistic model. Therefore, research has to be done towards the reactor, fuel cell, the load, the battery and the conversion steps. Most of the underlying principles are discussed in the first part of this research.

7.1.3. System boundary

'The system boundary is a trade off between simplicity, accuracy and computation time'[70]. Some simplifications are made for this system, while the most important components are taken into account to make sure the results are still accurate. An example of an simplification is the purity of the fuel and the quality of the water after filtering.

7.1.4. Model development

In the model development the elements inside the process are defined, as is illustrated in Figure 7.2.

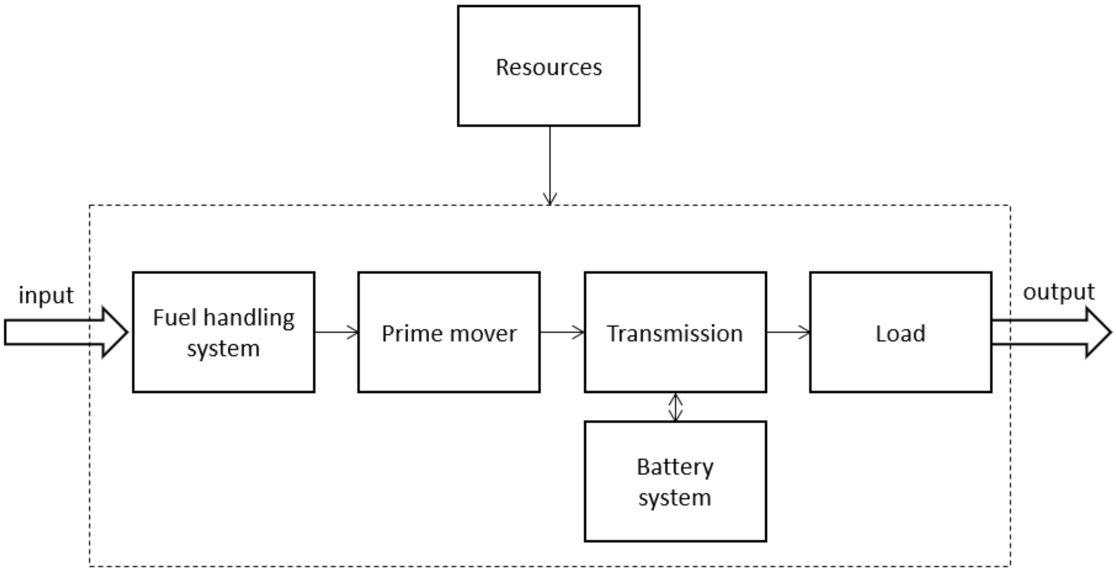

Figure 7.2: System overview of the simulation

In the *fuel handling system* the hydrogen generation from sodium borohydride is simulated. A mass flow of Sodium borohydride, water, and any type of accelerator are the most important input parameters of this sub-system. The output of the sub-system is a mass flow of hydrogen, a mass flow of the spent-fuel and heat.

For the *prime mover* a fuel cell system will be used to convert the mass flow of hydrogen in electricity. Parameters of a fuel cell suggested by Nedstack are used as input for the system. The dynamic behaviour of this system will also be an important factor on the systems dynamic behaviour.

In the subsystem *transmission* the available power will be distributed towards different users with different voltages. In this sub-system The DC-Bus, DC/DC-converters and other conversions are implemented.

The *load* on the system is defined by measurements on the current generators on-board of the ship. Multiple measurements are performed with variable loads in order to give a realistic representation of the most representative operational profile. Both long term and short term measurements are useful to test the performance.

The *battery system* is used as a variable subsystem to take care of the difference between the hotel load and the fuel cell power. The size of this system is dependent on the dynamic performance of the other systems.

7.1.5. Software

The simulation will be done in Matlab & Simulink. "Matlab is a high-performance language for technical computing. It integrates computation visualisation, and programming in an easy-to-use environment where problems and solutions are expressed in a familiar mathematical notation."[70] and Simulink is a graphical interface and a tool for simulating operational problems. In the Simulink model a system of differential-algebraic equations will be solved. Matlab and Simulink communicate with each other and can be used combined to build a model. Parts from the book "Modelling and simulation of systems using MATLAB and Simulink"[70] will be used as a starting point for the use of the program.

7.2. Simulation description

The model like build in Matlab Simulink is illustrated in Figure 7.3 and in more detail in Appendix G. Each subsystem build in this simulation will be discussed here.

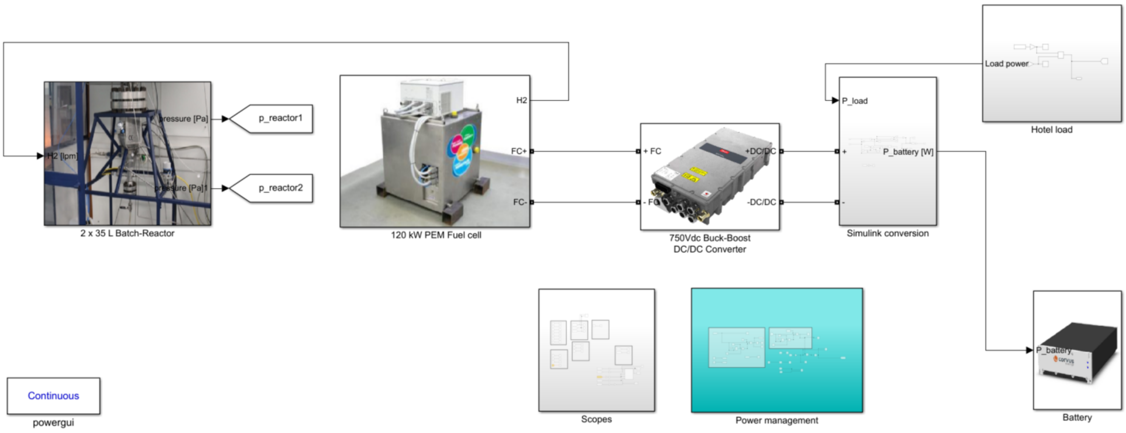

Figure 7.3: System overview of the simulation in Matlab & Simulink

7.2.1. Reactor

In the model a multi-purpose reactor is simulated. The reactor operates as a hydrogen generator and buffer. In this case an acid is used to accelerate the reaction, because this leads to the fastest reaction and is currently most developed. In the reactor subsystem of the model two 35 liter batch reactor are implemented. Both the $NaBH_4$-solution and the HCL are injected at the same time and react immediately according to a first order reaction. The reaction rate (k) is determined experimentally by determining the hydrogen generated from each batch. The hydrogen generation for one injection can be defined by Equation 7.1.

$$N(t) = N_0 \left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}} \tag{7.1}$$

Here, N is the concentration in mol, t the time in seconds and $t_{1/2}$ the half-life of the reaction in seconds. The behaviour of the reaction will result in a high hydrogen generation immediately after injection. Hereafter, the hydrogen generation will decrease rapidly. The longer the mixture stays in the reactor, the higher the hydrogen generation efficiency. This means the pressure will rise rapidly after injection and, therefore, the size of each injection is determined based on the pressure limit of the reactor.

Multiple fuel injections are used in one batch to increase the hydrogen generation efficiency and stay as compact as possible, like illustrated in Figure 7.4. The process starts with an almost empty reactor. Only a small amount of spent-fuel is left in the reactor to prevent a hydrogen flow trough the spent-fuel channels. The first fuel and HCL-injection is inserted and the hydrogen generation starts immediately and the pressure in the reactor rises. The hydrogen output flow can now be controlled.

The next injection can be controlled for injection-size or moment of injection, depending on the control system of the reactor. Both methods will be modelled. The injection is controlled by making use of pressure measurement in the reactor. A new injection can be started when, for example, the pressure drops down to a certain defined limit. This process continues until the reactor is filled with spent-fuel and the hydrogen pressure becomes to high. The reactor need to be emptied at this moment, in order to start the process all over again.

A big advantage of the injection method is that most of the spent-fuel has many time to complete or almost complete the reaction. During the last injection, all other injections have already had many time to release a big part of the hydrogen. In Equation 7.1 only the hydrogen generation of one injection is explained. In the reactor multiple injections act at the same time resulting in Equation 7.2,7.3 and 7.4.

$$N_{H_2}(p_1, p_2, ...) = N_1 \cdot k \cdot e^{-k \cdot p_1} + N_2 \cdot k \cdot e^{-k \cdot p_2} + N_3 \cdot k \cdot e^{-k \cdot p_3} + ... \tag{7.2}$$

$$N_{H_2}(p_1, p_2, ...) = \sum_{n_{batch}=0}^{n_{full}} N_0 \cdot k \cdot e^{-k \cdot p_n} \tag{7.3}$$

$$p = t_{start,injection} ... t_{end} \tag{7.4}$$

Here, p describes the time period (s) between the start of an injection until the time the reactor is emptied like explained in Equation 7.4

Assumptions are made in the model of this reactor. First of all, the injections are calculated separately and than summed up. In practice the fuels will mix with the spent-fuel in the reactor and the reaction rate will drop because the spent-fuel is a more basic solutions. This means the hydrogen generation takes place slower than calculated in this model. The fuels are, however, sprayed in the reactor in very small particles and because of the high concentration of HCL almost all hydrogen is already been generated before it mixes with the spent-fuel. Therefore, it is assumed that for this application this decrease in reaction speed can been neglected. This effect becomes more important when lower concentrations of HCL, or other accelerators, are used.

The pressure in the reactor affects the speed of the reaction. The reactor in this model is up to 100 bar. At this pressure the influence on the reaction speed is very small because the sodium borohydride and water are stored in a compact solid or liquid. This effect is, therefore, neglected in the model.

The reactor is full when the spent-fuel and the hydrogen generation together goes to the pressure limit of the reactor. Multiple parameters can be varied when a signal of a full reactor is given . First of all, the time between the last injection and emptying the reactor can be varied. The longer this period, the more hydrogen can be generated and, therefore, a higher hydrogen generation efficiency can be met. A disadvantage of a long waiting time is that no extra hydrogen is generated during this process. This can, however, partly be solved by implementing a second reactor, which runs twice as fast, while the other reactor is in its emptying process. A second parameter, which can be varied, is the hydrogen flow out of the reactor during this period. There is a buffer of hydrogen in the reactor-tank, but since no extra injection can be realised this buffer decreases while emptying the reactor tank. To prevent a to low pressure in the tank and, therefore, a to small hydrogen buffer, the second reactor can be used by increasing its hydrogen flow while the other reactor is waiting. The amount of flow during while emptying a reactor can be optimised in the model.

In the model two reactors are used for two reasons. First of all, the reactor will not be able to deliver the requested hydrogen flow at high loads when one reactor is emptied. A second reactor is, therefore, needed to deliver an extra hydrogen flow. The second reason to use multiple reactors is due to the fact that it becomes easier to deliver a constant flow. The overall pressure difference becomes lower and the hydrogen generation is better divided over the time because of the first order characteristics of the reaction. This effect is also illustrated in Figure 7.5. The pressure peaks become lower, when more reactors are used. Therefore, a less complex reactor design is required because the pressure limit is lower. With more reactors it also becomes easier to maintain a more constant pressure.

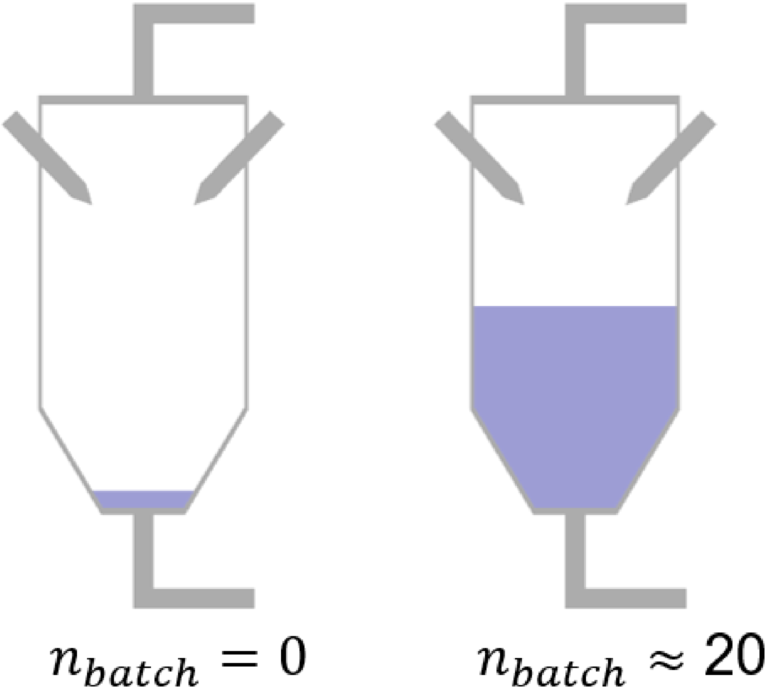

Figure 7.4: Working principle of a multi-purpose acidic reactor used in the model

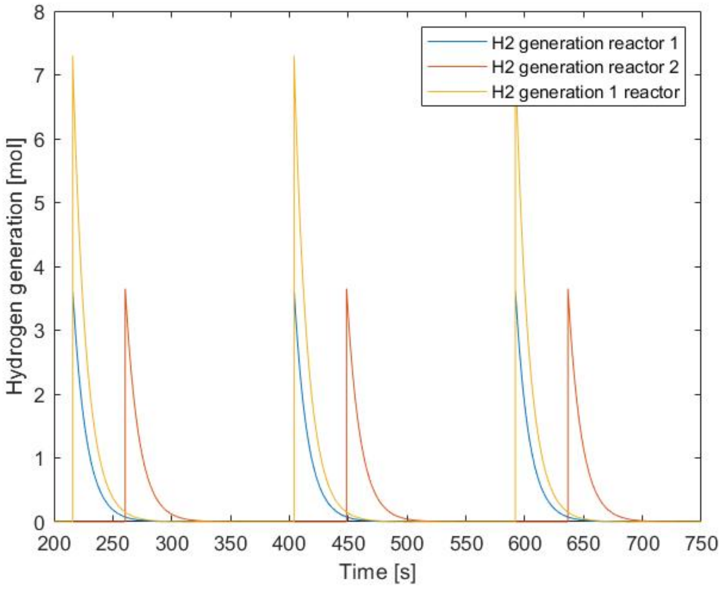

Figure 7.5: Hydrogen generation of two separate reactors vs. one reactor

7.2.2. Fuel cell

The standard model of the Matlab & Simulink Powersystems-pack is used for the fuel cell. In this model a PEMFC is used. The characteristics of a cell can be implemented in this system. In this model several variable signals can be used as input. Depending on the relevant information needed for the simulation output, the level of detail can be determined. In this case, especially the hydrogen flow to the fuel cell is important, because this affects the hydrogen flow from the reactor. The air flow and pressure, for example, are less relevant for the purpose of this model. These variables are assumed to be controlled by the model itself.

The hydrogen flow is controlled by making use of a flow rate regulator, which measures a reference current just after the fuel cell. The current is converted to a hydrogen flow required. The calculation from current to flow is illustrated in Equation 7.5.

$$\dot{V} = \frac{60 \cdot 1000 \cdot R \cdot T \cdot N_c \cdot I_{ref}}{2 \cdot F \cdot p_{fuel} \cdot p_0 \cdot U_f \cdot c_{H_2}} \tag{7.5}$$

Where R is the gas constant, T the operating temperature, N_c the number of cells, I_{ref} the reference current, F the constant of Faraday, p_0 the atmospheric pressure, U_f the fuel utilisation and c_{H_2} the hydrogen composition.

The dynamic behaviour of the the fuel cell is defined by the time from 10% to 100% of its power output. This parameter is defined by the fuel cell manufacturer. At higher power fluctuation the flow change of hydrogen becomes to high and can damage the cell. Therefore, a flow rate limiter is implemented in the model. This means the main delaying factor of the fuel cell is based on this limiter. The difference need to be supplied by batteries or capacitors when the power demand exceeds this limit.

7.2.3. Transmission

From the fuel cell a variable voltage and current is produces depending on the flows through te cell. The converter transforms this to a constant voltage and a variable current to the DC-bus. It is assumed that the converter directly converts the voltage to the DC-Bus voltage because the conversion step is not the most delaying factor in the drive train. This assumption is also made for the conversion-steps after the DC-bus. The losses, however, are significant and, therefore, the average loss of 2% for each conversion is taken into account, like also mentioned in Chapter 4. The other conversion losses can be found to and from the battery and to the load.

7.2.4. Battery

The battery system in the model is used to improve dynamic behaviour and can possibly be used for peak-shaving. When, for example, the load has high fluctuations the battery can be used to cover the difference between the fuel cell limit and the load. The size of the battery is dependent on the maximum amount of power asked from the system and for peak-shaving the amount of energy needed during a peak. As will also be mentioned in Chapter 8, only the heavy load fluctuations are relevant for this specific application. This means the C-rate will become an import results from the battery subsystem. The C-rate is calculated in Equation 7.6.

$$C-rate = \frac{I[A]}{C_{rated}[Ah]} \tag{7.6}$$

Where I is the charge or discharge current in Ampere and C_{rated} the energy stored in the battery [Ah]. When, for example, the capacity is 10 [Ah] and the current 5 [A], the C-rate becomes 2C and it will take half an hour to charge or discharge the battery. High C-rates will damage the battery and, therefore, charging or discharging too fast needs to be prevented. Normally the manufacturer of the battery will give an advise for an operating range of a maximum and minimum C-rate. This means the dynamic behaviour improves when more battery-capacity is installed on-board of the vessel.

7.2.5. Load

The load is the environmental impact on the system. Examples of different kind of loads are: the hotel load, the propeller and an auxiliary load. In this model this power load is the result of a measurement on-board of the vessel. The load can, however, easily be changed to analyse the systems dynamic behaviour of other load types. On this application the load is measured just after the DC-bus and conversion losses after the DC-bus are, therefore, already taken into account.

7.2.6. Power management system

In the power management system all data measured from the subsystems are combined to control the system and to make sure the load matches with the other subsystems. One of the most important measurement is the pressure in the reactor, because this is used to monitor the hydrogen buffer in the system and, therefore, the timing and size of injection. Another important control parameter is the fuel regulator, which has to deliver the right amount of hydrogen to the fuel cell if the reactor is capable to deliver this flow. As already mentioned, this flow regulator is limited, resulting in the possibility that the control of the reactor is not enough to match the load on-board of the vessel.

A battery control system is modelled to cover the load in case of high fluctuations or when peak-shaving is implemented. This system covers for the difference between the load and the power supply of the fuel cell. When, for example, the fuel cell supplies 60 kW and the demand is 70 kW, the battery systems delivers 10 kW. The battery also need to be charged and, therefore, the state of charge (SOC%) is measured. The management system sends out a signal when the SOC is becoming to low or to high. In this case, the fuel cell and reactor need to deliver more or less power for a certain amount of time to charge/discharge the batteries.

Multiple methods of energy management can be compared In the model. At first, the fuel cell will deliver a constant load together with the reactor. In this power management strategy the reactor can easily be designed for an optimal hydrogen generation efficiency with a constant period between each injection. This means that the difference between the load and the fuel cell need to be covered by the battery systems. In the second method, the fuel cell will follow the load to minimise the use of the battery system. In this case, also the reactor can't deliver a constant hydrogen flow and, therefore, a variable injection time is used to improve the dynamic behaviour. Results on both methods are illustrated and discussed in Chapter 8 and 9.

8

Simulation input

A model to study the dynamic behaviour of the drive train is now made and the specific applications can be tested. In this chapter the Clipper Stad Amsterdam (CSA) is analysed for implementation of an sodium borohydride-system for the hotel-load on-board of the vessel. First, the CSA is described and thereafter the characteristics of the other subsystems are reported.

8.1. De Stad Amsterdam

The CSA is a sailing passenger vessel sailing mainly on the Caribbean, Mediterranean and the North Sea. The main dimensions of the vessel are reported in Table 8.1. In this research a feasibility study for the implementation of a sodium borohydride system is done in collaboration with DAMEN Bergum. Results of the first part of this thesis are used to investigate the options on-board of the vessel. This new design is tested on volume, weight, lay-out and safety. Results of this study can be found in Appendix F.

Three scenarios are considered for the CSA . The first one only includes an electrification of the drive train to a DC-bus, and the possibility to produce power from the propeller during sailing. The second scenario, illustrated in Figure 8.1, is the same as the first besides the hotel load of the vessel which is covered by a fuel cell and sodium borohydride reactor. In the third scenario, all energy required for the hotel load and propulsion is produced by fuel cells and a sodium borohydride reactor. All scenario's considered in the study can be found in Appendix F. The study resulted in a combination of scenario one and two. In this option the hotel load is generated by a sodium borohydride application in the harbour conditions only. In this case the system is placed next to the ship on the land, resulting in a silent solution, free from harmful emissions in harbour conditions.

Scenario two can be simplified to a reactor, fuel cell, DC-Bus, battery and load. The load is also the input for the simulation of this system. Measurements on the generators installed on the vessel have been done during a trip to give a realistic overview of the systems behaviour. The power supplied by the generators, which normally cover the hotel load, are measured. The first measurement is illustrated in Figure 8.2. This is a measurement over a period of 180 seconds. In this measurement the change of the load is clearly illustrated. Multiple users are activated during the measurement to give a realistic fluctuation of the load. In this case anchor winches were activated resulting in peaks around 100 kW. The long-term measurement is can be found in Figure 8.3 where the power demand is measured each hour for 79 hours in total. Both measurements are providing an useful insight of the behaviour of the hotel/auxiliary load on-board of the CSA.

The load can change heavily and a power range between 40 and 110 kW can be expected. The short-term measurement is used in the model to analyse load fluctuation in the range of seconds. This can, for example, be the acceleration of a vessel, a bow thruster or like for this measurement, the power fluctuation of the hotel load and auxiliary systems. In the long-term measurement the power stays continuous for one hour and than changes to another level. This measurement is used to analyse the emptying procedure of the reactor, the battery control system, the fuel consumption and the efficiencies of the subsystems.

Table 8.1: Main characteristics of the CSA

Clipper de stad Amsterdam		
Name	Stad Amsterdam	
Call sign	PECA	
Flag	the Netherlands	
Homeport	Amsterdam	
Owner	Randstad Clipper Beheer BV & Amsterdam Clipper beheer BV	
Type	Sailing passenger vessel	
Builder	Damen Oranjewerf Amsterdam	
Designer	Gerard Dijkstra, NBJA, Amsterdam	
Main Dimensions	**[m]**	
Lpp	55.85	
Ltc	56.18	
Lod	60.5	
Loa	66.56	
Los	76	
Bmax	10.5	
Depth	6.45	
Draft forward	4.75	
Draft aft	4.85	
Air draft	46.85	
Other characteristics		
Displacement	1038	ton
Gross tonnage	723	ton
Net tonnage	277	ton
Max sail area windward	1900	m^2
Max sail area running	2200	m^2
Main engine	749	kW
Type	Caterpillar 3508 V8	
2 Generators	2x156	kW
Type	Caterpillar 3306	
Cruising speed engine power	10	kt
Hull speed under sail	17	kt
Fresh water	30000	l
Fuel	42500	l

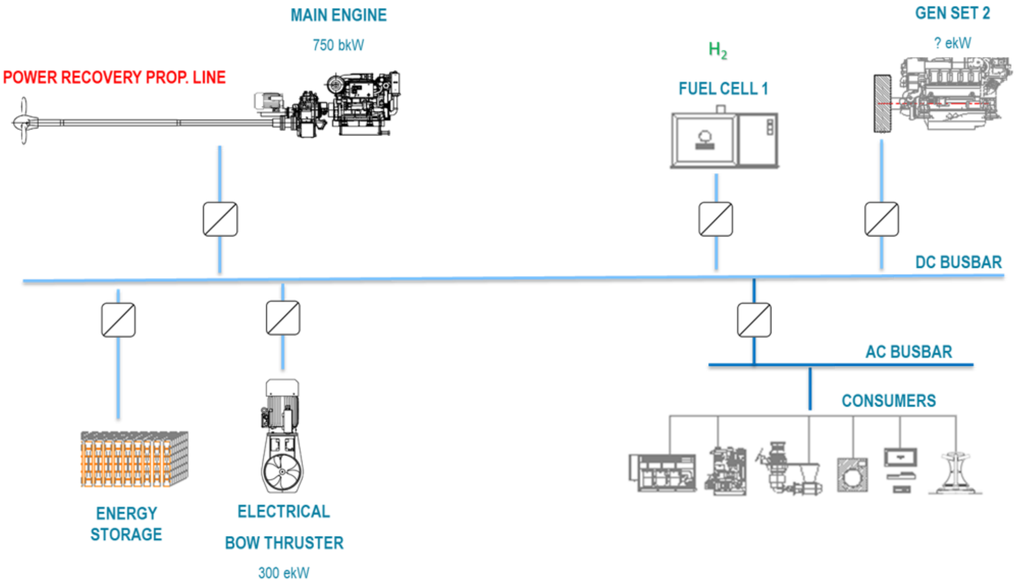

Figure 8.1: Feasiblity study scenario 2, CSA

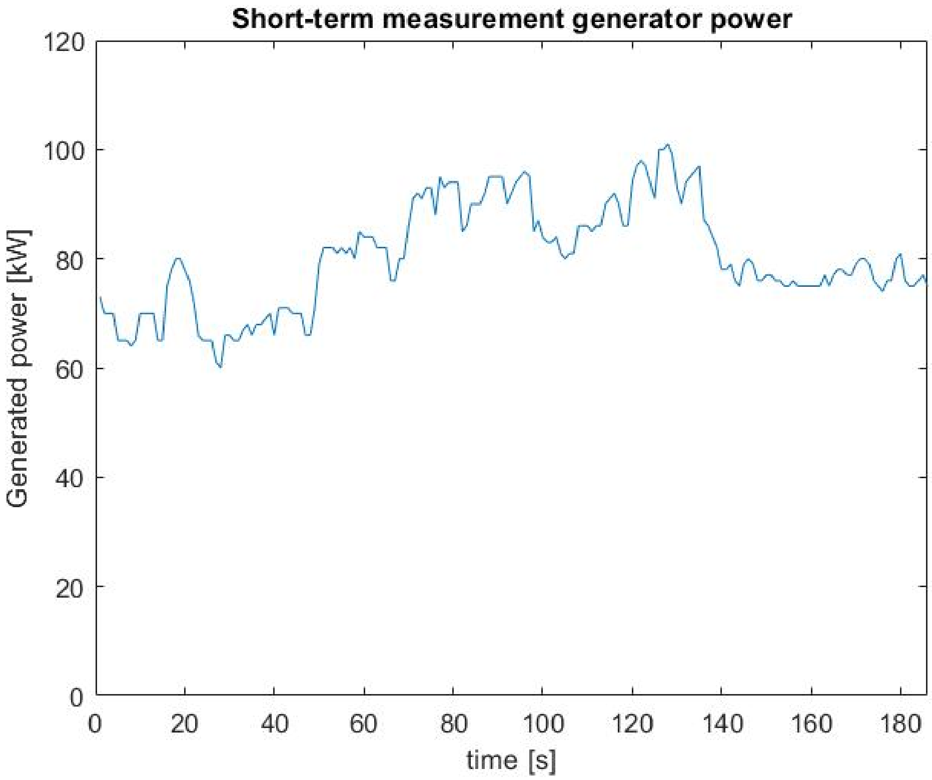

Figure 8.2: Short term measurements on the CSA

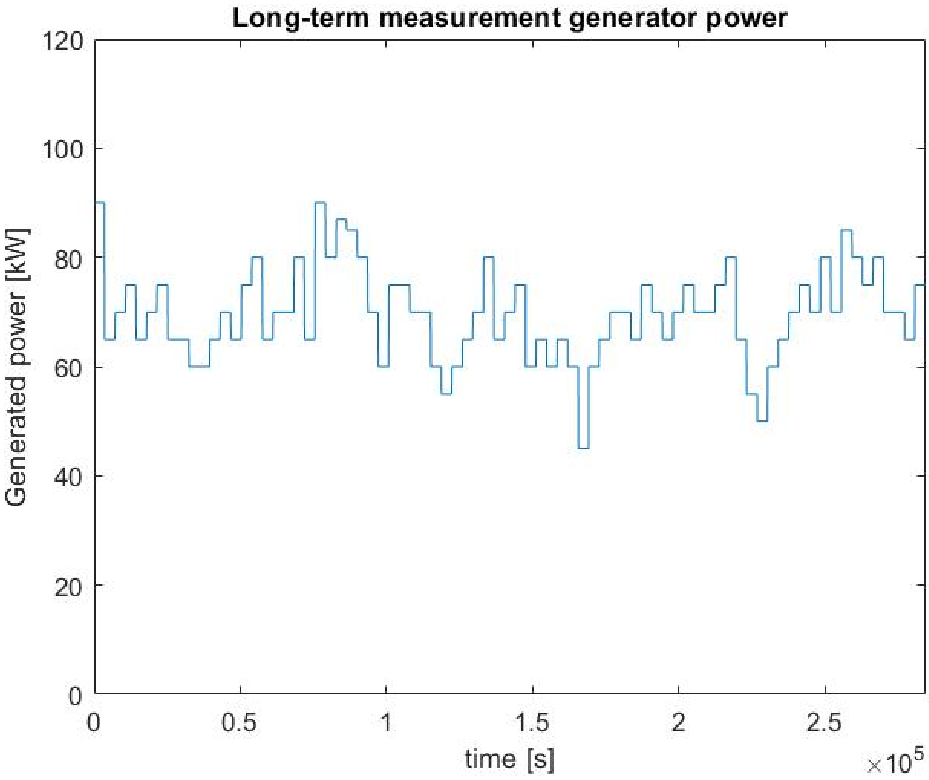

Figure 8.3: Long term measurements on the CSA

8.2. Fuel cell input

For the feasibility study on the CSA a Nedstack fuel cell module of 100 kW (operating point) is used for the simulation. The measurements reveals that this level is just barely exceeded. At higher power demands, the fuel cell can still deliver power till 160 kW. This results, however, in lower efficiencies. The input needed for the Powersim fuel cell model is obtained by Nedstack. Most important input parameters, including the dynamic behaviour of the fuel cell, can be found in Table 8.2 and Figure 8.4

Table 8.2: Nedstack input parameters for the fuel cell subsystem

Parameters	
Nominal operating point	120 [A], 838 [V]
Maximum operating point	230 [A], 690 [V]
Number of cells	1200
Nominal stack efficiency	55 [%]
Operating temperature	65 [°C]
Fuel cell response time	10 [s]
Flow regulator	I_{ref} [A]

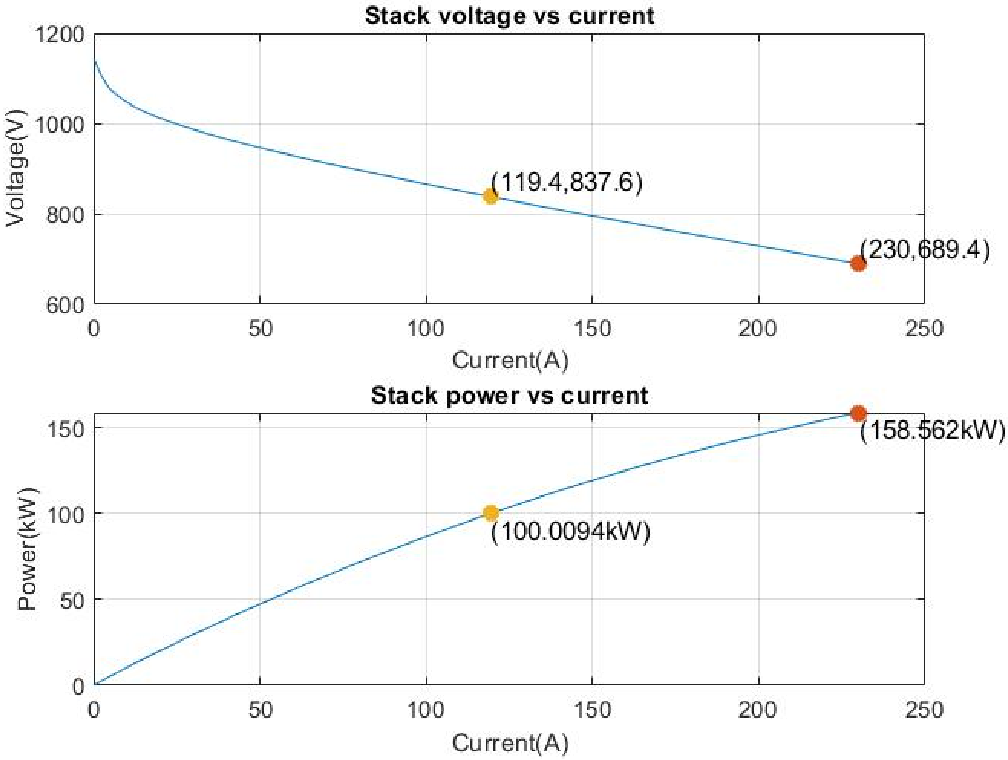

Figure 8.4: I-V curve of the fuel cell suggested by Nedstack

The maximum operating point of the cell is much higher than the 100 kW mentioned before as can be seen in the fuel cell input parameters. This is mainly to minimize the situations in which the fuel cell operates at maximum power, because this decreases the life time of the cell. The other reason is that the degradations of the cell is already taken into account. This ensures that also after 20.000 hours the 100 kW can still be reached by the stack. The cell needs to be replaced after 10% degradation in efficiency, as is defined by the manufacturer.

8.3. Battery-pack

Damen Bergum analysed multiple types of batteries and also the capacity on-board of the vessel. In this model a Corvus Lithium ion battery system is used. The C-rates, explained in Chapter 7, are in this case -2.5 C and 2.5 C. It is preferable to stay in this range while charging or discharging. The capacity of the batteries on-board are less relevant for this drive-train, because the batteries on the CSA are also used for storage of energy generated from the propeller in sail-mode, and to assist the bow thruster. This will result in an oversized battery-pack for the hotel load only. The capacity will, therefore, be changed to a more representative value for the hotel load only. This is also a result of the simulation, to conclude the minimum capacity needed for the hotel load.

9

Results and Analysis

The model and input is described in Chapter 7 and 8. Both the results and analysis of the model simulations are illustrated and reported in this chapter. Thereby, an answer to the last sub-question can be provided: How does the system behave on a transient load on one specific configuration of the 'Clipper de Stad Amsterdam'? The dynamic behaviour of the system proposed for the CSA is reviewed on its performance. Besides this specific application a relation or conclusions for more general applications can be drawn.

9.1. Variable batch size

First, the constant time between each injection is simulated and the size of the injection is varied. More fuel and hydrochloric acid is injected in the reactor when a higher energy demand is required, like when the battery needs to be charged. For the short-term simulation most import results are illustrated in Figure 9.1, where the load, pressure, fuel cell power and battery power are included. As is illustrated in the figure, the battery covers the difference between the load and fuel cell. The C-rate of a 92 kWh battery-system is illustrated in Figure 9.2.

A period of 6000 seconds for the power management is shown in Figure 9.3 for the long term measurement. Reactor 1 is emptied one time and reactor 2 is emptied two times in this period. The ratio between the hydrogen inserted in the reactor and the hydrogen flow out of the rector is shown in Figure 9.4. The limit of the graph goes to the total hydrogen generation efficiency of the reactor.

The fuel cell runs in this simulation constant and, therefore, doesn't have any influence on the dynamic behaviour. This means the reactors have to deliver a constant flow of hydrogen. The reaction rate is, however, not constant. Therefore, a buffer of at least one injection in hydrogen gas is designed in the model.

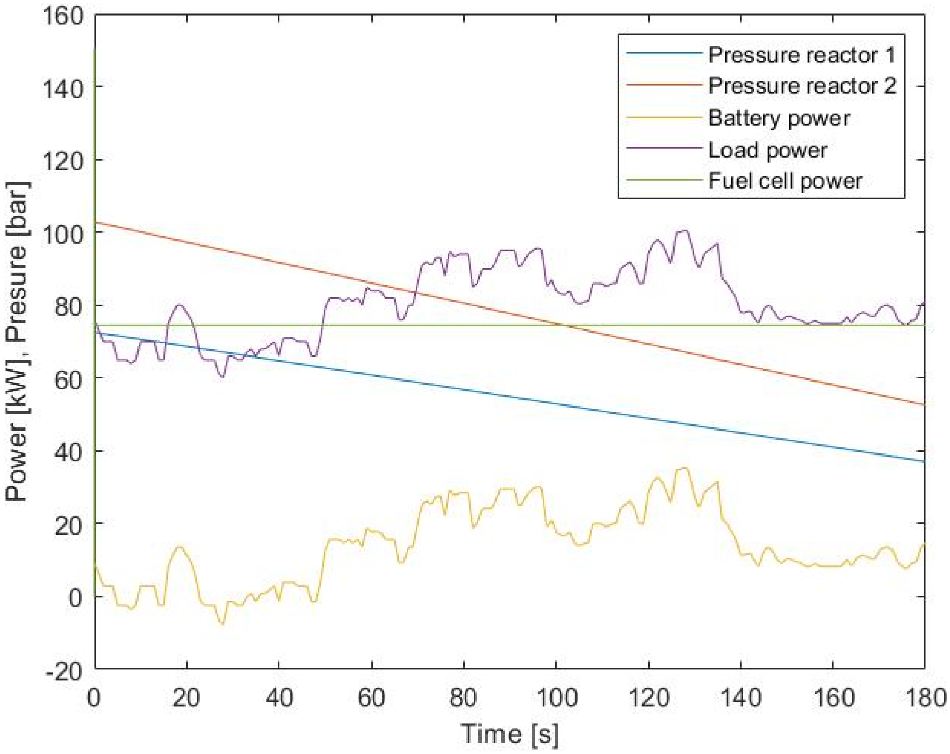

Figure 9.1: Power management using a variable batch size (short term)

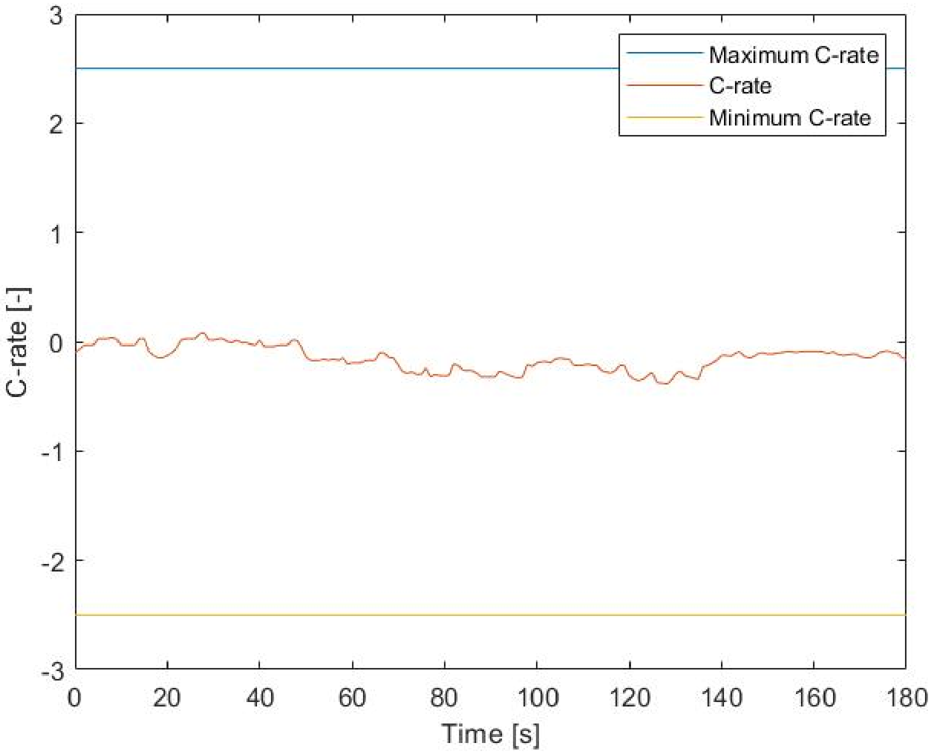

Figure 9.2: C-rates using a variable batch size (short term)

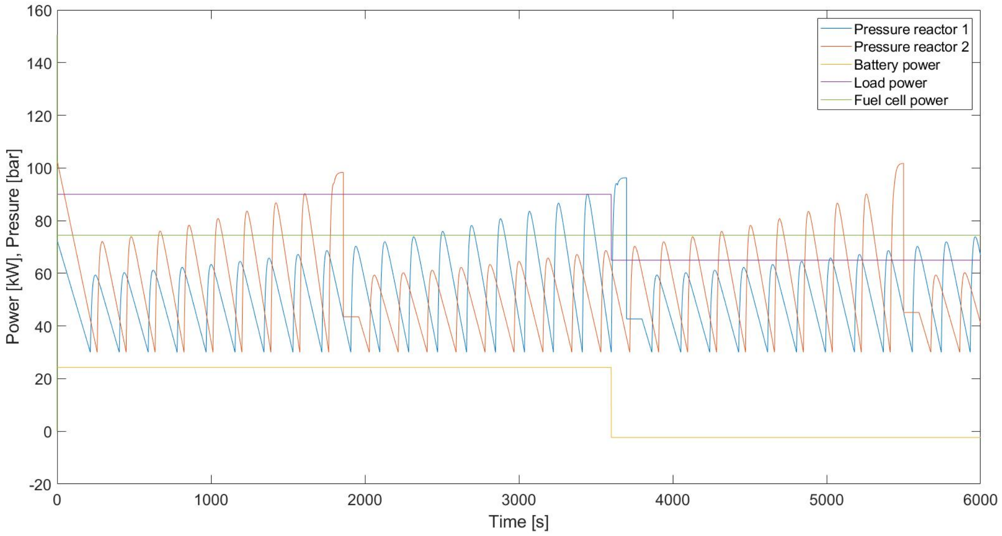

Figure 9.3: Power management using a variable batch size (long term)

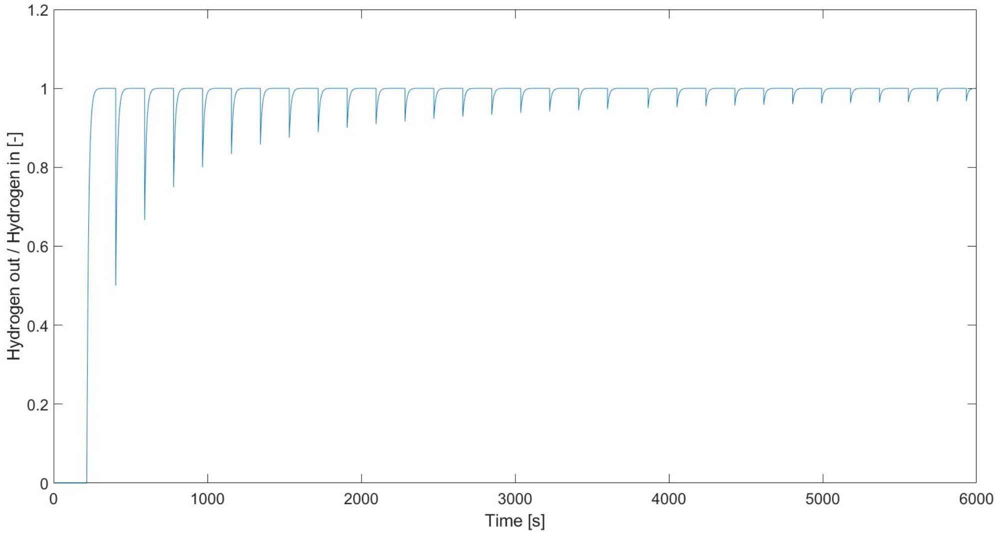

Figure 9.4: Total hydrogen generated over the hydrogen injected in the reactor with a variable batch size (long term)

In the short-term measurement no fuel injection takes place, because there is still enough hydrogen in the reactor. Only the hydrogen buffer is used in this case and so the pressure drops linear for a constant fuel cell power.

The range of the battery is -30 - +40 kW because the fuel cell delivers 70 kW. The C-rate of the battery becomes higher because the fuel cell is running constant. As can be seen in Figure 9.2, the C-rate does not exceed the limit of charging or discharging and can, therefore, 'easily' manage the load fluctuations of the system. The capacity of the battery is, however, 92 kWh or 184 Ah at 500 V, resulted from the feasibility study in Appendix F. The minimum size of the battery can be determined by calculating back from the C-rates defined by the manufacturer. The maximum current becomes 80 A since the maximum power demand is 40 kW at 500 V and with a C-rate of 2.5 this results in a minimum rated capacity of 33 Ah. The behaviour of this battery is illustrated in Figure 9.5.

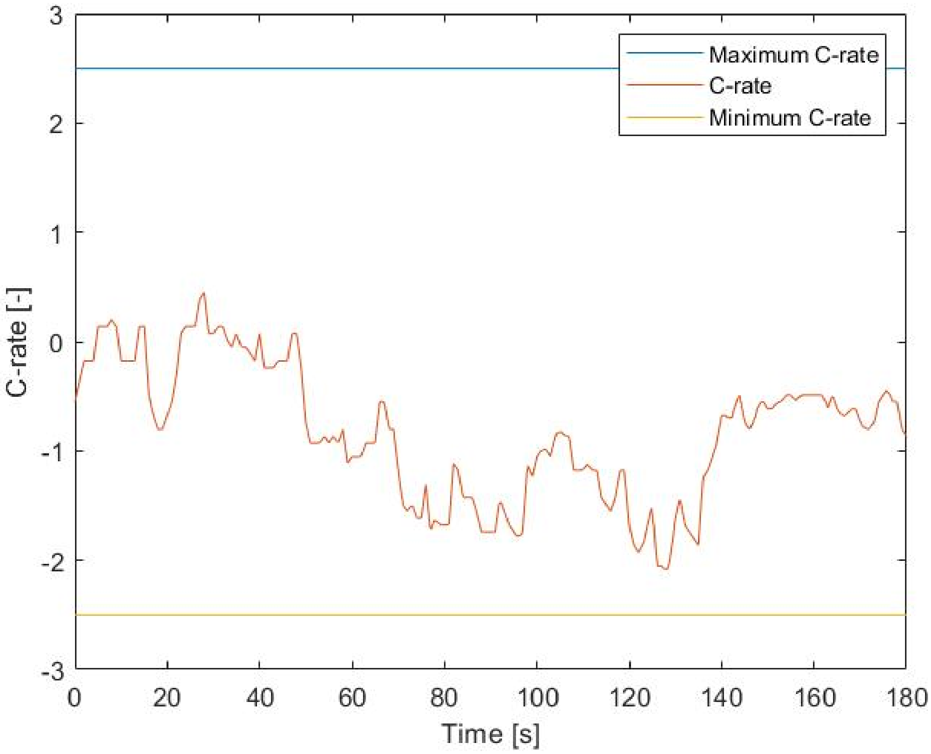

Figure 9.5: C-rates using a variable batch size, optimised battery size (short term)

The behaviour of the reactors can be analysed in the long term simulation. Figure 9.3 clearly shows the constant period between each injection. The pressure in the reactor increases for every new injection because the space for the hydrogen buffer decreases while the spent-fuel volume increases. After 1800 seconds, reactor 2 sends out a signal that the tank is full. After the signal the reactor waits for an, in the design determined, amount of time. Thereafter the pressure drops, because the reactor is emptied and the hydrogen flow can run again. The first fuel injection takes place again when the pressure drops below the defined limit (in this case 30 bar). This result demonstrates that the buffer of the two reactors is high enough to deliver a hydrogen flow for a constant power of $70kW$. The limit of the hydrogen output over the hydrogen input goes to a value just below the 100%, which is also representative for reactors which are already in use [64]. The proposed battery system can deliver the rest of the power and covers the load fluctuations measured on the CSA.

9.2. Variable injection time

The same simulation is done for the variable injection time shown in Figure 9.6, 9.7, 9.8 and 9.9. The fuel consumption is also calculated for the total period of 79 hours, shown in Figure 9.10. The tank level of Fuel 50, the 30 wt.% HCL-solution (A30) and the spent-fuel over time is shown in this figure.

The method of using a constant fuel cell load and a constant time between injection has the advantage that the reactor can be optimised for a optimal hydrogen generation efficiency. A disadvantage, however, are the losses in the battery system. The energy to the battery need to be converted to 500 V first with a loss around 2%. There are also some losses by charging/discharging the battery itself (10-20%) and when the energy is needed again, there is the same loss again in the conversion to the DC-bus. This means the total energy storage loss can go up 24%, which is a significant value to further take in consideration. Another disadvantage, not shown in the results, is the moment when the size of the injection is increased. The pressure in the reactor exceeds its limit much earlier when more fuel is injected at once because of the characteristics of the reaction. For this reason it becomes interesting to look at the opportunity to let the fuel cell follow the load as much as possible, and vary the injection time to improve the dynamic behaviour of the reactor. Therefore, the variable injection time is also simulated and analysed on its feasibility and performance.

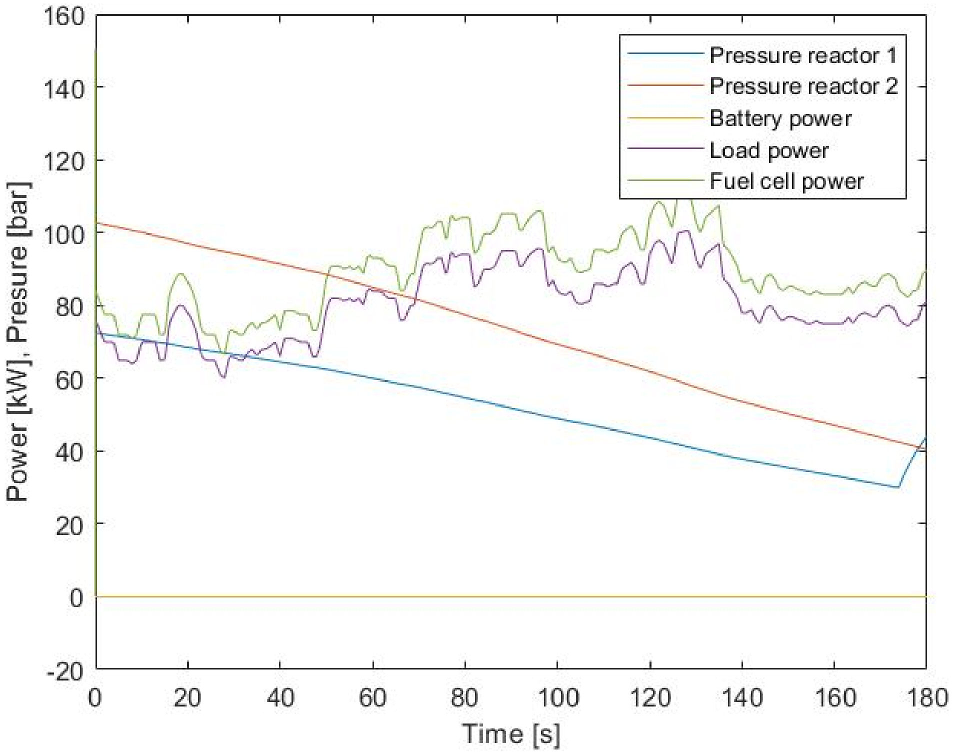

Figure 9.6: Power management using a variable injection time (short term)

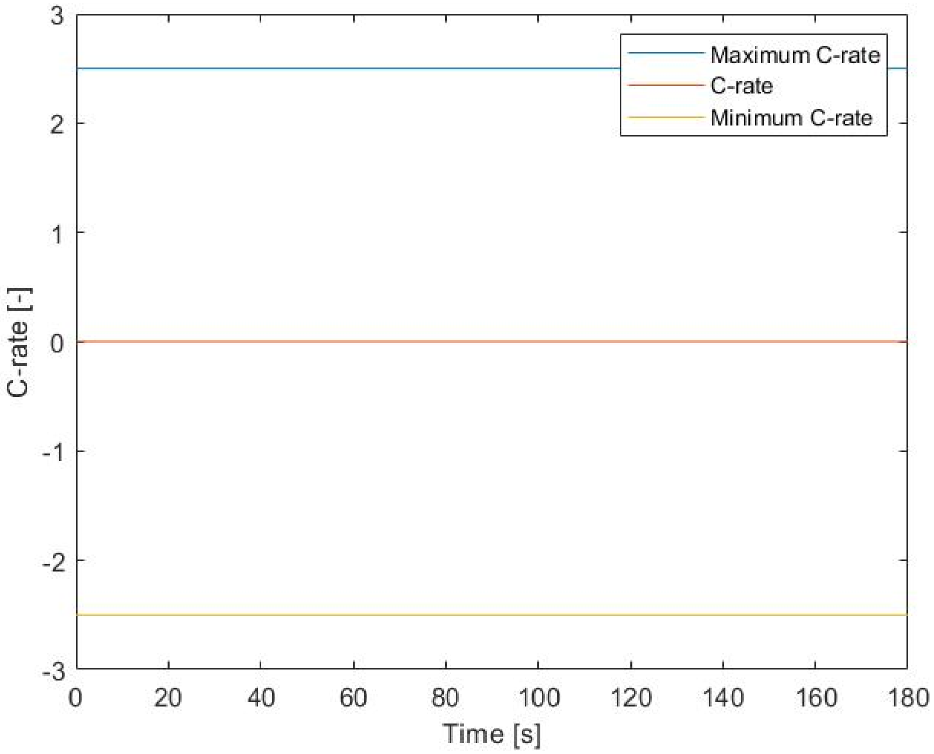

Figure 9.7: C-rates using a variable injection time (short term)

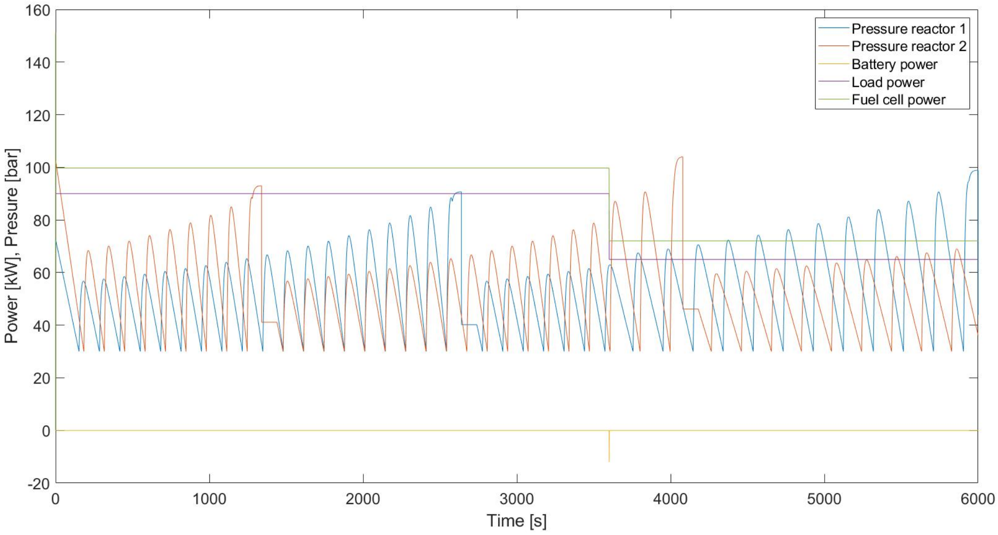

Figure 9.8: Power management using a variable injection time (long term)

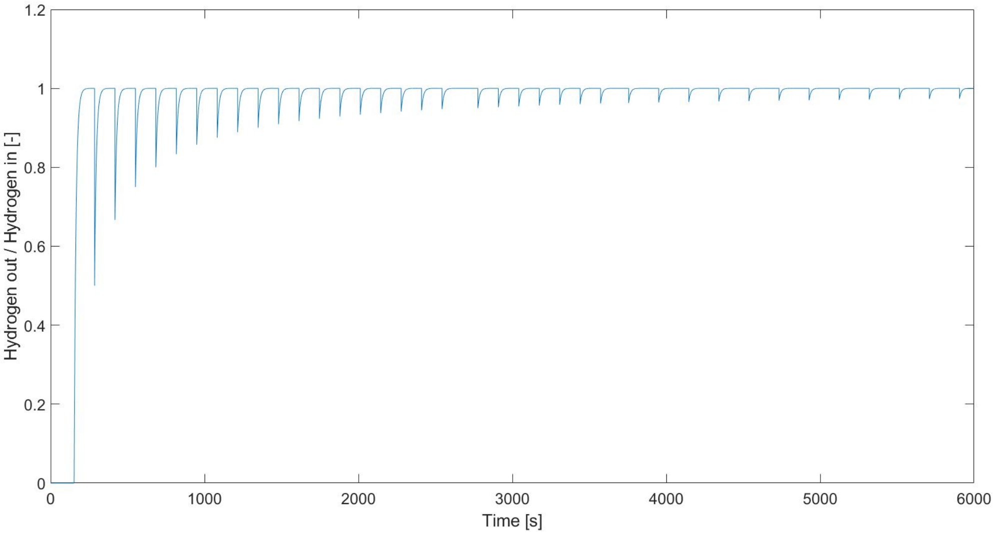

Figure 9.9: Total hydrogen generated over the hydrogen injected in the reactor with a variable injection time (long term)

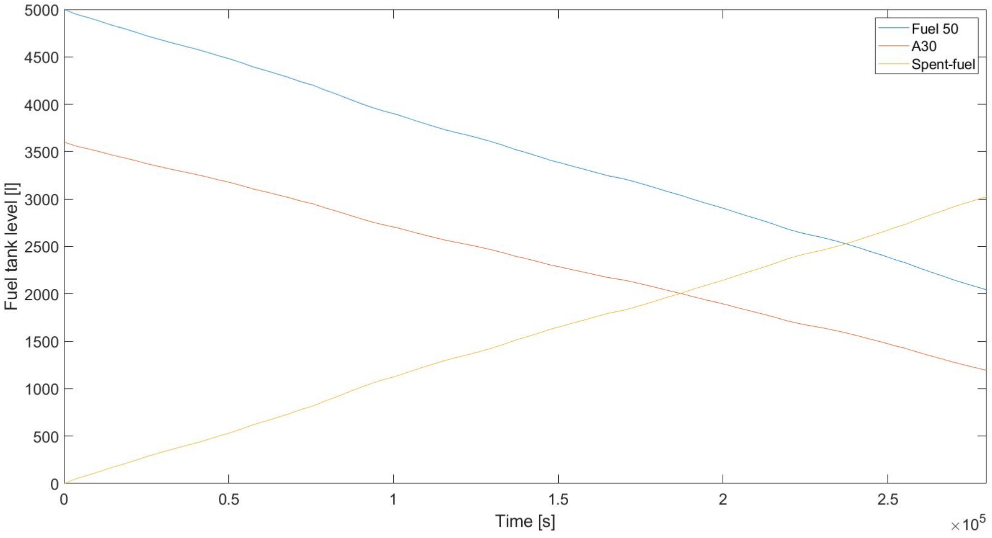

Figure 9.10: Fuel consumption and spent-fuel generation (long term)

In the results, Figures 9.6, 9.7, 9.8 and 9.9 show an overview of this method. On the short term simulation it is clearly shown that this fuel cell is capable to follow the load fluctuation. For this period the battery doesn't need to be used. The difference between the load and the fuel cell power is due to the losses in the conversion after the fuel cell. The pressures in the reactors fluctuates in this case more, because the flow varies. For example, when the second anchor winch is turned on between 120 and 140 seconds the pressure decreases more rapidly. From Figure 9.6 it can be concluded that the hydrogen buffer in the reactors is big enough to regulate a flow-difference between 60 and 110 kW. Around 175 seconds, the pressure rises rapidly again because of a new injection is taking place.

In the long-term simulation the variable injection time is clearly shown when the load changes. At a lower load, the period between injections becomes longer after one hour. The reactors are capable to deliver the right amount of hydrogen following the load on-board of the vessel, within the pressure range the reactor is designed for. This hydrogen buffer is also high enough for the required hydrogen flow for the full simulation of 79 hours. The most important question is, however, whether the hydrogen generation efficiency will be effected negatively. This limit is shown in Figure 9.9, which is also getting close to the 100% like in the previous method. Only a small difference is measured at high power demands in the 79 hour simulation. This difference is due to the fact that fuels has a shorter time to complete the reaction. The difference is, however, relatively small because of the method of using multiple injection in a reactor. In this reactor 20 injections can be stored. The reaction of the first 19 injections is almost fully completed, even when the power demand is high. This results in a negligible difference in hydrogen generation efficiency for this method, with a much better performance on dynamic behaviour and a minimal use of the battery system. This results in a higher system efficiency since the use of the battery system, with high energy losses, is minimised.

9.3. Other applications and configurations

The results of the simulations show that the system proposed for the CSA is capable supply the required amount of power to the load. Most important factors leading to this result are the buffers implemented in the drive train. Both, the hydrogen buffer and the battery size can be optimised to match the operational profile on-board of a vessel. It is advisable to only use a small battery-system and a sufficient hydrogen buffer for this application. The reactor doesn't become the delaying factor in the drive train anymore when enough hydrogen is stored. In this case the limiter on the fuel cell determines the capability of operating at a fluctuating load and, therefore, the capacity of the battery.

These conclusions may not be the same for other maritime application. It could be advisable to implement a smaller fuel cell and hydrogen generation system, and a bigger battery-system when for example, peak-shaving becomes of higher importance. The balance between hydrogen buffer, battery or even supercapacitors should be reconsidered when the load fluctuates more heavily. Here efficiency of the systems, size and cost are becoming important parameters.

The acid activator will become a challenge in the maritime industry from safety perspective, as is also explained in Chapter 6. Therefore, it is advisable to consider a catalytic reactor, which changes the reactor model significantly. The reaction time of a catalyst is much longer and, therefore, a bigger reactor is needed. The system will reacts slower to load fluctuation due to the slower reaction time. This means the hydrogen buffer need to be increased to satisfy the hydrogen demand. The size of the battery can be reconsidered when the size of the reactor increases to much. Another option to improve the dynamic behaviour is to use more, smaller, catalytic reactors to generate a more continuous flow and to have the option to refill a reactor without too many efficiency losses.

9.4. Conclusions

A model is built for the hotel and auxiliary load on the CSA to test how a sodium borohydride system on-board of a vessel performs. Both, a continuous fuel cell load together with a battery system and a fluctuating load on the the fuel cell, are simulated. The first measurement on the CSA is used to analyse the performance of the system in a fluctuating load on the short-term and the second measurement is done to analyse the system on the long-term.

Two reactors are optimally designed to generate a continuous hydrogen flow to the fuel cell combined with a continuous load on the fuel cell. The hydrogen generation efficiency of the reactor is close to 100% because multiple injections are stored in the reactor until its full. The efficiency becomes higher by increasing the time till emptying the reactor. The battery in this system is used to cover the difference between the load and the fuel cell power. A downside of this method is that energy is lost in conversion and heat by making use of the battery.

The use of the battery in minimised by letting the fuel cell follow the load. The fuel cell is limited to a maximum hydrogen flow change. Therefore, the battery system is still used to cover the difference. The fuel cell suggested for the CSA is, however, designed to follow the load of the measurements easily. The reactors in this method have a variable injection time. A new injection takes place when the pressure drops below a certain value. On high loads over a long time the system can still generate the right amount of hydrogen and, therefore, follow the hotel and auxiliary load of the CSA, without a significant drop in efficiency. The other reactor can be used to generate a higher hydrogen flow when one reactor is full.

It can be concluded from the model that the most important factors determining the performance on dynamic behaviour are the hydrogen buffer in the reactors, the flow rate through the fuel cell and the size of the battery. Depending on the type of application these factors can be varied to optimise the design on size, weight, efficiency and cost. For an application like the CSA a load following fuel cell with a sufficient hydrogen buffer, and just a small battery system will satisfy the requirements. The results may be different when, for example, peak-shaving becomes more interesting, or the load fluctuates more heavily.

III

Conclusions and recommendations

10

Conclusions and recommendations

10.1. Conclusions

10.1.1. Sodium borohydride systems

A fuel handling system on sodium borohydride can be implemented using many types of fuels and configurations. The water used in this process will, however, lead to a high volume and weight of the fuels. The energy density of this system is in the range of 32 - 39 kg/kgH_2 and 30 - 45 l/kgH_2. A 30 wt.% $NaBH_4$-solution and an unfiltered spent-fuel is used in this case.

There are several ways to make the system more compact when volume or weight are becoming critical elements in the design of such a system . A volume-exchange tank will increase the energy density when both, the fuel and spent-fuel are stored in the same tank. A more concentrated $NaBH_4$-solution or spent-fuel results in a more compact and complex system. The water needed for the reaction has to be produced by the fuel cells, or by making use of reverse osmosis on-board the vessel. The most compact and light configuration can be realized by making use of a dry $NaBH_4$-powder, produce the water on-board, partly filter the water out of the spent-fuel and by implementing a volume-exchange tank. The energy density of this configuration is in the range of 12 - 14 kg/kgH_2 and 7 - 11 l/kgH_2.

The results of the power density of the configurations are close to each other. Most important factor in the power density is the size of the reactor. The other components in the system are relatively small. For most applications in the maritime industry a catalytic reactor is the most logical choice. The power density lies in a range of 7 - 32 l/kW and 7 - 33 kg/kW, expressed in the potential chemical energy in hydrogen.

10.1.2. Fuel cells

Fuel cells have many advantages for the maritime industry. The compact, efficient modules are improving the energy and power density of the system. The emission of NO_x can be decreased significantly by using a low temperature cell in comparison with an ICE. When hydrogen is used as a fuel also the CO_2 and SO_x emissions are eliminated. Other advantages are high performance in part-load and a silent system.

The LT-PEMFC, HT-PEMFC and the SOFC are considered for this drive train . The PEMFCs results in a compact and efficient solution, operating at low temperatures. The life-time of this fuel cell is proven to be sufficient for the use in the maritime industry. The LT-PEMFC is very sensitive to impurities in the fuel, which is partly solved by using a HT-PEMFC. The efficiency of a HT-PEMFC is, however, much lower and the system is less compact. The LT-PEMFC would be a better solution for a sodium borohydride solution because the quality of the hydrogen from the reactor is high enough.

The SOFC operates at higher temperatures. In general a much bigger system is required for a module like this. The efficiency of the SOFC, however, is higher than a PEMFC and waste heat recovery can be implemented more easily. Depending on the application both systems has its advantages and disadvantages. One of the most import factor is the combination of the power density and the energy density of the system.

10.1.3. Other system components

A DC-bus on-board of a vessel has some advantages for this system. Since the fuel cell and batteries are operating at DC, the conversion to and from the bus becomes more efficient. From safety perspective, however, some extra measures has to be taken to get control over the current in case of an emergency.

Normally, a battery system is needed besides the fuel cell. The battery is used for high load fluctuations and can be used for peak-shaving. A power management system needs to make sure the fuel cell and battery supplies the right amount of power to the loads. The size and type of the battery-system is depends on the operational profile of the vessel and the capability of the fuel cell to follow the load. Lithium-ion and lead acid batteries are the most used batteries in the maritime industry, because of its high power and energy density and its high availability. Super-capacitors can be considered for an even better dynamic behaviour.

A control system need to be implemented to match each subsystem of the drive train. Important measurements controlling the system are: the reactor pressure, the fuel cell reference current, the DC-bus voltage and the load power.

10.1.4. Power and energy density

The most compact solution, in terms of energy density, is heavy compared to fuels like diesel, LNG and methanol. Especially in the end of the trip when all spent-fuel is produced, the weight of the vessel increases. In comparison with liquid or compressed hydrogen the total system gravimetric energy density performs slightly better.

Looking at the volume of the system, the concept of the dry fuel and filtered spent-fuel performs very well compared to other alternative fuels, such as methanol, LNG and compressed or liquid hydrogen. A general diesel fuel handling system is, however, much more compact. This, mainly because of the fact that the spent-fuel need to be stored on-board of the vessel and the tank-systems are estimated larger and heavier than, for example, an integrated diesel tank.

The energy density is not the only parameter which determines the size and weight of the whole system. The power density of the system need to be added up to the energy density in order to determine the total size and weight. This is, however, different for each type of application and, therefore, these two are combined in Ragone charts. From these plots some important conclusions can be drawn. In the most compact case of a $NaBH_4$-configuration, the volume of the system is comparable with a diesel system. The system can even be more compact until trips around 10 operating hours. Until 200 hours, the system volume is still close to the volume of a diesel system. Hereafter, the difference becomes more significant.

There is a point where the SOFC-system becomes more compact or lighter than a PEMFC-system because of the SOFC has a higher efficiency. For the gravimetric density this point lies around 250 operating hours, and for the volume around 1000 operating hours, using the optimum densities. Therefore, from system density point of view, the SOFC becomes interesting to consider for long trips.

It can be concluded that the power density of the compressed hydrogen system is much higher compared to a $NaBH_4$-system. The fuel has, however, a much lower energy density, especially looking at the volume. The $NaBH_4$-system becomes more compact between 10 and 50 operating hours.

10.1.5. Safety

It can be concluded that the use of hydrochloric acid is a big challenge from safety perspective. Therefore, the options to use a catalyst instead of an acid is highly recommended for the future use of these systems. Research towards this accelerator is already planned and might make the system more realistic to implement on vessels. Other hazards are: fire and explosion hazards from the hydrogen released by the fuels, in the mix chamber and in the fuel cell. Sufficient detection, protection and prevention need to be taken into account to secure the safety on-board.

10.1.6. Dynamic behaviour

A model is built for the hotel and auxiliary load on the CSA to test how a sodium borohydride system on-board of a vessel performs. Both, a continuous fuel cell load together with a battery system and a fluctuating load on the the fuel cell, are simulated. The first measurement on the CSA is used to analyse the performance of the system in a fluctuating load on the short-term and the second measurement is done to analyse the system on the long-term.

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The use of the battery in minimised by letting the fuel cell follow the load. The fuel cell is limited to a maximum hydrogen flow change. Therefore, the battery system is still used to cover the difference. The fuel cell suggested for the CSA is, however, designed to follow the load of the measurements easily. The reactors in this method have a variable injection time. A new injection takes place when the pressure drops below a certain value. On high loads over a long time the system can still generate the right amount of hydrogen and, therefore, follow the hotel and auxiliary load of the CSA, without a significant drop in efficiency. The other reactor can be used to generate a higher hydrogen flow when one reactor is full.

It can be concluded from the model that the most important factors determining the performance on dynamic behaviour are the hydrogen buffer in the reactors, the flow rate through the fuel cell and the size of the battery. Depending on the type of application these factors can be varied to optimise the design on size, weight, efficiency and cost. For an application like the CSA a load following fuel cell with a sufficient hydrogen buffer, and just a small battery system will satisfy the requirements. The results may be different when, for example, peak-shaving becomes more interesting, or the load fluctuates more heavily.

10.2. Recommendations

As is concluded the concepts of the sodium borohydride system has a high potential for the maritime industry. Looking at the current state of technology, however, still many research need to be done to prove the concepts and make sure the systems can be implemented safely on this scale. Multiple scenario's have been tested on their performances in this research, and from these results some recommendations for the development of this technology follow. On some of the subjects in this research a higher level of detail should be studied before the system is implemented on-board of a vessel.

It can be concluded that the water needed for the process is a challenge looking at the gravimetric and volumetric energy density study of this research. Several options to increase this density are studied. It is, therefore, recommended that these opportunities need to be developed and studied further to prove a working concept on a large scale. Tests need to be done on, for example, the volume-exchange tank and the filtering system of the spent-fuel.

The reactor has proven to be a big component in the system. Many reactor-designs are possible and many improvements can be made on this scale. Development and research towards the reactor-design will, therefore, be of high importance for the future implementation of this system in the maritime industry. These will automaticly result in a more precise estimation of the power density of the system.

Looking at the safety of the system, many research still has to be done. Since there are no regulations for these systems on-board of vessels, challenges has to be overcome before the system can be used. To secure the safety various stakeholders need to work together and several iteration steps need to be made.

The simulation offers an useful estimation of the performance in dynamic behaviour of the system. Some assumption are made in this model, which can be studied further. In this case it is, for example, assumed that the reaction is a first order reaction. In practice a somewhat faster reaction will take place, affecting the reactor pressure and the dynamic behaviour of the system. It is highly recommended to make the same model for a catalytic reactor, because of the safety issues related to the use of a HCL-solution.

Not or, just barely mentioned in this research are the cost and environmental impact of this system. A study on these subjects will be needed before implementing a system like this. The operational costs of the system are highly dependent on the regeneration process, which is still at a lower technology readiness level than the system on-board of the vessel. It is recommended to do a financial feasibly study, besides this technical feasibility study, when this technology is further developed.

Looking at the results of this research, it can be concluded that this technology has a high potential for many types of applications in the maritime industry. It will be technically feasible to implement a system like this on-board of a vessel. Moreover, the maritime sector even has some advantages in comparison with other markets. The harmful emission in this industry can be decreased significantly using this system. Cost and safety of the system are, however, a challenge and, therefore, further research has to be done to realise the implementation of these systems on-board of vessels.

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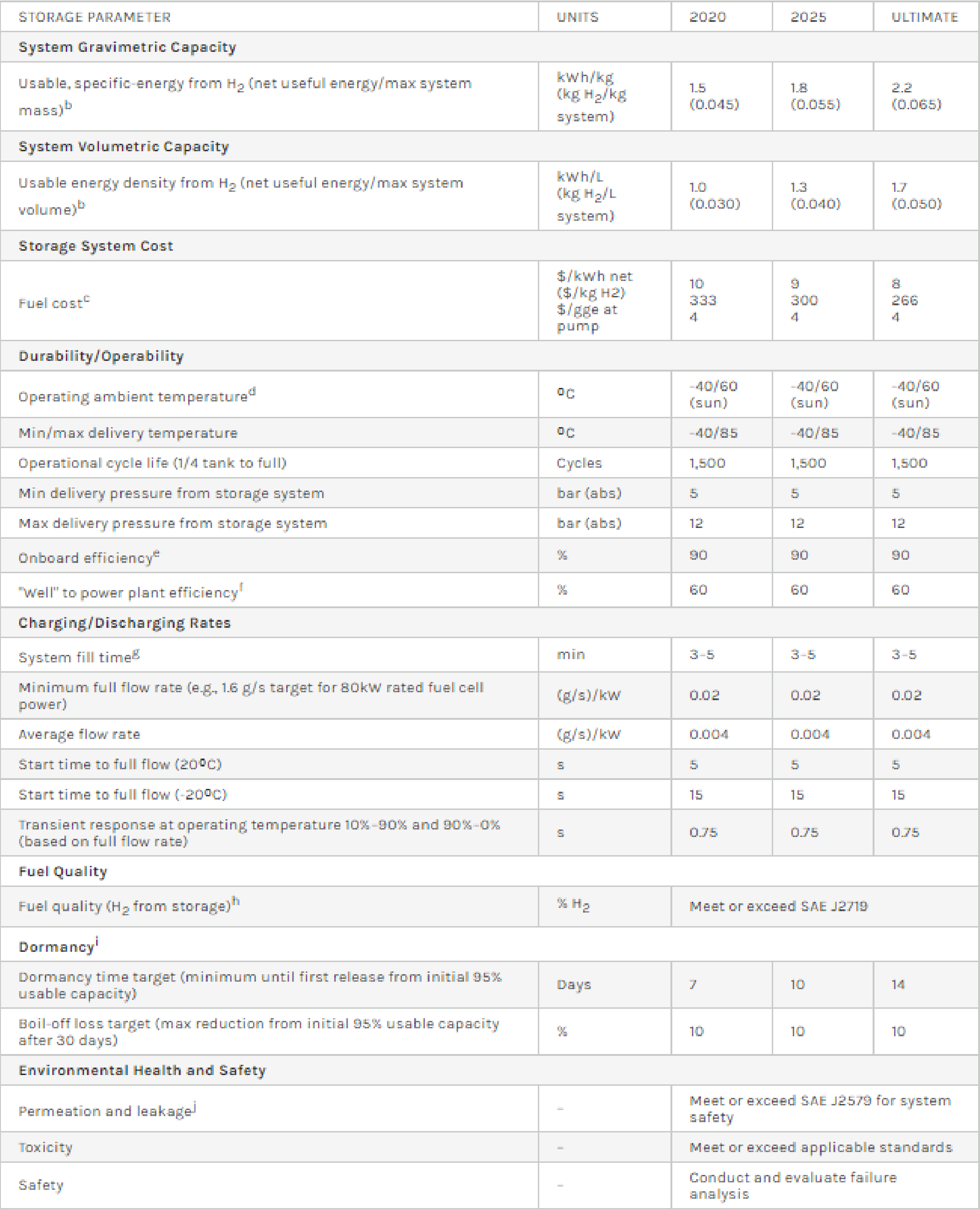
A

Appendix A: DOE targets

Table A.1: Technical system targets: On-board hydrogen storage for light-duty Fuel Cell vehicles [2]



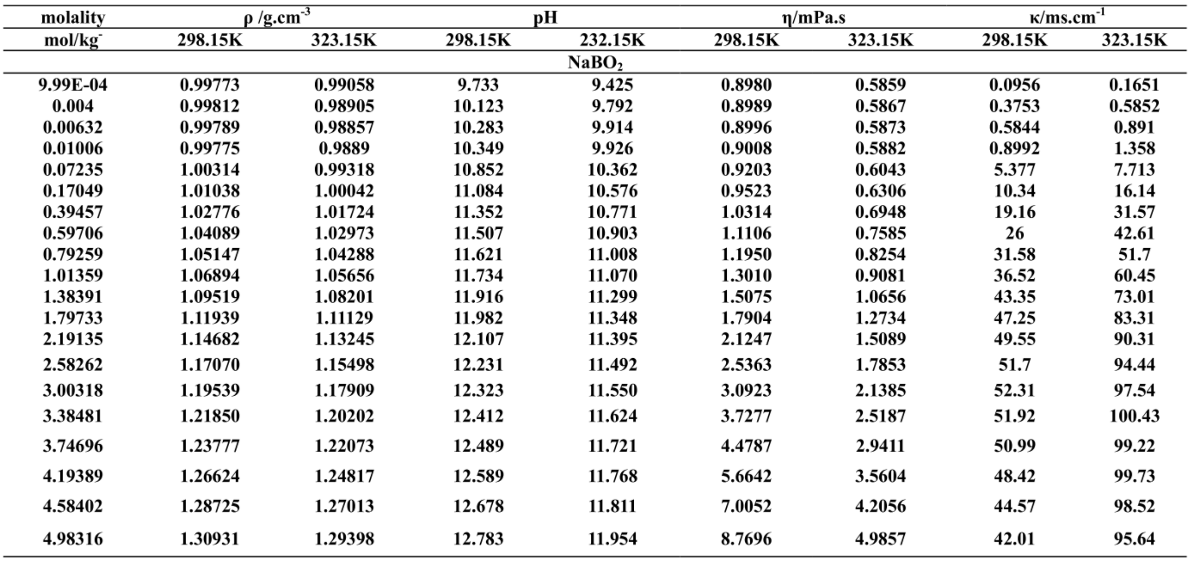
STORAGE PARAMETER	UNITS	2020	2025	ULTIMATE
System Gravimetric Capacity				
Usable, specific-energy from H_2 (net useful energy/max system mass)[b]	kWh/kg (kg H_2/kg system)	1.5 (0.045)	1.8 (0.055)	2.2 (0.065)
System Volumetric Capacity				
Usable energy density from H_2 (net useful energy/max system volume)[b]	kWh/L (kg H_2/L system)	1.0 (0.030)	1.3 (0.040)	1.7 (0.050)
Storage System Cost				
Fuel cost[c]	\$/kWh net (\$/kg H2) \$/gge at pump	10 333 4	9 300 4	8 266 4
Durability/Operability				
Operating ambient temperature[d]	°C	-40/60 (sun)	-40/60 (sun)	-40/60 (sun)
Min/max delivery temperature	°C	-40/85	-40/85	-40/85
Operational cycle life (1/4 tank to full)	Cycles	1,500	1,500	1,500
Min delivery pressure from storage system	bar (abs)	5	5	5
Max delivery pressure from storage system	bar (abs)	12	12	12
Onboard efficiency[e]	%	90	90	90
"Well" to power plant efficiency[f]	%	60	60	60
Charging/Discharging Rates				
System fill time[g]	min	3-5	3-5	3-5
Minimum full flow rate (e.g., 1.6 g/s target for 80kW rated fuel cell power)	(g/s)/kW	0.02	0.02	0.02
Average flow rate	(g/s)/kW	0.004	0.004	0.004
Start time to full flow (20°C)	s	5	5	5
Start time to full flow (-20°C)	s	15	15	15
Transient response at operating temperature 10%-90% and 90%-0% (based on full flow rate)	s	0.75	0.75	0.75
Fuel Quality				
Fuel quality (H_2 from storage)[h]	% H_2	Meet or exceed SAE J2719		
Dormancy[i]				
Dormancy time target (minimum until first release from initial 95% usable capacity)	Days	7	10	14
Boil-off loss target (max reduction from initial 95% usable capacity after 30 days)	%	10	10	10
Environmental Health and Safety				
Permeation and leakage[j]	-	Meet or exceed SAE J2579 for system safety		
Toxicity	-	Meet or exceed applicable standards		
Safety	-	Conduct and evaluate failure analysis		

B

Appendix B: Chemical Properties

Table B.1: Chemical properties sodium borohydride [11, 16, 46]

Sodium borohydride		
Molecular Formula	BH_4Na	
Description	White crystal powder	
Mol mass	37.83	g/mol
Melting point	400	°C
Boiling point	500	°C
Density	1.035	g/mL at 25 °C
Flashing point	70	°C
Water solubility	550	g/L at 25 °C
ΔH	-188.6	KJ/mol
ΔG	-123.9	KJ/mol
°S	101.3	J/mol/K
C_p	86.8	J/mol/K



molality	**ρ /g.cm^{-3}**		**pH**		**η/mPa.s**		**κ/ms.cm^{-1}**	
mol/kg^{-}	**298.15K**	**323.15K**	**298.15K**	**232.15K**	**298.15K**	**323.15K**	**298.15K**	**323.15K**
				$NaBO_2$				
9.99E-04	0.99773	0.99058	9.733	9.425	0.8980	0.5859	0.0956	0.1651
0.004	0.99812	0.98905	10.123	9.792	0.8989	0.5867	0.3753	0.5852
0.00632	0.99789	0.98857	10.283	9.914	0.8996	0.5873	0.5844	0.891
0.01006	0.99775	0.9889	10.349	9.926	0.9008	0.5882	0.8992	1.358
0.07235	1.00314	0.99318	10.852	10.362	0.9203	0.6043	5.377	7.713
0.17049	1.01038	1.00042	11.084	10.576	0.9523	0.6306	10.34	16.14
0.39457	1.02776	1.01724	11.352	10.771	1.0314	0.6948	19.16	31.57
0.59706	1.04089	1.02973	11.507	10.903	1.1106	0.7585	26	42.61
0.79259	1.05147	1.04288	11.621	11.008	1.1950	0.8254	31.58	51.7
1.01359	1.06894	1.05656	11.734	11.070	1.3010	0.9081	36.52	60.45
1.38391	1.09519	1.08201	11.916	11.299	1.5075	1.0656	43.35	73.01
1.79733	1.11939	1.11129	11.982	11.348	1.7904	1.2734	47.25	83.31
2.19135	1.14682	1.13245	12.107	11.395	2.1247	1.5089	49.55	90.31
2.58262	1.17070	1.15498	12.231	11.492	2.5363	1.7853	51.7	94.44
3.00318	1.19539	1.17909	12.323	11.550	3.0923	2.1385	52.31	97.54
3.38481	1.21850	1.20202	12.412	11.624	3.7277	2.5187	51.92	100.43
3.74696	1.23777	1.22073	12.489	11.721	4.4787	2.9411	50.99	99.22
4.19389	1.26624	1.24817	12.589	11.768	5.6642	3.5604	48.42	99.73
4.58402	1.28725	1.27013	12.678	11.811	7.0052	4.2056	44.57	98.52
4.98316	1.30931	1.29398	12.783	11.954	8.7696	4.9857	42.01	95.64

Figure B.1: Density, Conductivity, pH and viscosity of aqueous $NaBO_2$ solutions as function of concentration at 298.15 and 323.15 K [49].

Table B.3: Chemical properties sodium hydroxide [11, 16, 46]

Sodium hydroxide		
Molecular Formula	$NaOH$	
Description	White crystal powder, acid neutraliser	
Mol mass	39.997	g/mol
Melting point	323	°C
Boiling point	1388	°C
Density	2.13	g/mL at 25 °C
Flashing point	-	°C
Water solubility	1090	g/L at 20 °C
ΔH	-425.6	KJ/mol
ΔG	-379.5	KJ/mol
°S	64.5	J/mol/K
C_p	59.5	J/mol/K

Table B.4: Chemical properties hydrogen [11, 16, 46]

Hydrogen		
Molecular Formula	H_2	
Description	Colourless gas	
Mol mass	2.02	g/mol
Melting point	-259.2	°C
Boiling point	-252.8	°C
Density	0.0899	g/L at 0 °C
Flashing point	500	°C
Water solubility	0.0017	g/L at 25 °C
ΔH	0.0	KJ/mol
ΔG	-	KJ/mol
°S	130.7	J/mol/K
C_p	28.8	J/mol/K

Table B.2: Chemical properties sodium metaborate [11, 16, 46]

Sodium metaborate		
Molecular Formula	$BNaO_2$	
Description	Sodium salt	
Mol mass	65.798	g/mol
Melting point	966	°C
Boiling point	1434	°C
Density	2.464	g/mL at 25 °C
Flashing point	-	°C
Water solubility	36	g/L at 35 °C
ΔH	-977.0	KJ/mol
ΔG	-920.7	KJ/mol
°S	73.5	J/mol/K
C_p	65.9	J/mol/K

Table B.5: Chemical properties ultra pure water [11, 16, 46]

Ultra pure water		
Molecular Formula	H_2O	
Description	Colourless liquid	
Mol mass	18.015	g/mol
Melting point	0	°C
Boiling point	100	°C
Density	0.995	g/ml at 25 °C
Flashing point	-	°C
Water solubility	-	g/L at 25 °C
ΔH	-285.8	KJ/mol
ΔG	-237.1	KJ/mol
°S	70.0	J/mol/K
C_p	75.3	J/mol/K

C

Appendix C: Subcomponents fuel handling system

Table C.1: Reverse Osmosis systems

Model No.	**GPD**	**LPD**	**l/s**	**Width [m]**	**Depth [m]**	**Height [m]**	**Volume [m^3]**	**m3/l/s**	**Weight [kg]**	**kg/l/s**	**Power [kW]**	**Power [kW/l/s]**	**m3/kW**	**kg/kW**	**Cite**
Maritime 150	150	567	0.007	0.64	0.48	0.32	0.097	14.84	50	7619	0.65	99.05	0.15	76.92	[40]
Maritime 300	300	1135	0.013	0.64	0.48	0.32	0.097	7.41	52	3958	0.75	57.09	0.13	69.33	[40]
Maritime 400	400	1514	0.018	1.12	0.48	0.32	0.171	9.76	60	3424	0.95	54.21	0.18	63.16	[40]
Maritime 800	800	3028	0.035	1.12	0.51	0.46	0.260	7.42	65	1855	1.40	39.95	0.19	46.43	[40]
Maritime 1200	1200	4542	0.053	1.12	0.51	0.46	0.260	4.95	70	1332	1.50	28.53	0.17	46.67	[40]
Maritime 1600	1600	6056	0.070	1.12	0.51	0.46	0.260	3.71	80	1141	2.10	29.96	0.12	38.10	[40]
Aqua matic 450-1	450	1703	0.020	0.71	0.31	0.42	0.094	4.76							[54]
Aqua matic 1800-2	1800	6814	0.079	1.19	0.34	0.42	0.171	2.17							[54]

Result	min	max
Volume [m3/l/s]	2.17	14.84
Weight [kg/l/s[	1141.35	7619.05
Power [KW/l/s]	28.53	99.05

Table C.2: Ultra pure water systems

Name	**W [m]**	**D [m]**	**H [m]**	**V[m^3]**	**Weight [kg]**	**Flow Rate [L/min]**	**Flow rate [l/s]**	**kg/l/s**	**m3/l/s**	**cite**
Aurora Crysta Series 1000	0.50	0.36	0.54	0.10	25	2.00	0.03	750.00	2.92	[8]
Aurora Crysta Series 2000	0.50	0.36	0.54	0.10	25	2.00	0.03	750.00	2.92	[8]
PURELAB® Chorus 1 Type I Ultrapure Water System	0.38	0.34	0.44	0.06		2.00	0.03		1.66	[8]
Super-Q® Plus Water Purification System	0.80	0.22	1.15	0.20	63	12.00	0.20	315.00	1.01	[41]
PURELAB CHORUS 1 TYPE I Ultrapure water System from ELGA Labwater	0.38	0.34	0.44	0.06		2.00	0.03		1.66	[36]
Barnstead E-Pure Type 1 Ultrapure Water Purification Systems from Thermo Fisher Scientific	0.74	0.19	0.71	0.10		2.50	0.04		2.40	[36]
Barnstead LabTower EDI Type 1 Water Purification system from thermo fisher scientific	0.45	0.58	1.50	0.39		30.00	0.50		0.78	[36]

Results	min	max
Volume [m3/l/s UPW]	0.78	2.92
Weight [kg/l/s UPW]	315.00	750.00

Table C.3: High pressure reactors

Fixed Bed reactors	Inner volume [L]	W	D	H	V	m^3/L inner	Weight [kg]	kg/L inner	Cite
High pressure stirred lab autoclaves / reactors	10	1.31	0.585	1.155	0.885134	0.088513			[22]
	20	1.31	0.585	1.7	1.302795	0.06514			[22]
	25	1.31	0.585	1.8	1.37943	0.055177			[22]
	50	1.5	0.675	2.35	2.379375	0.047588			[22]
	100	1.5	0.78	2.35	2.7495	0.027495			[22]
Parr Instrument company Series 4540	0.6	0.5334	0.7112	1.6002	0.607042	1.011737	79.379	132.2983	[14]
	1.2	0.5334	0.7112	1.6002	0.607042	0.505869	83.91	69.925	[14]
Parr Instrument company Series 4570	1.8	0.508	0.7574	1.905	0.732966	0.407203	129.28	71.82222	[14]
Parr Instrument company Series 4580	3.75	0.508	0.7574	1.905	0.732966	0.195458	156.49	41.73067	[14]
	5.5	0.508	0.7574	1.905	0.732966	0.133267	170.097	30.92673	[14]

Results	**min**	**max**
Volume [m3/L inner]	0.027495	1.011737
Weight [kg/L inner]	30.92672727	132.2983

Table C.4: Fuel storage tanks

Name	**L [m]**	**W [m]**	**H [m]**	**V[m^3]**	**Weight [kg]**	**Capacity [L]**	**Price**	**cite**
IBC vat, IBC container of IBC tank van 1000 liter op stalen pallet met aftapkraan	1.2	1	1.16	1.39	59	1000	€ 330.00	[15]
IBC vat, IBC container of IBC tank van 1000 liter op houten pallet met aftapkraan	1.2	1	1.16	1.39	66	1000	€ 310.00	[15]
IBC vat, IBC container of IBC tank van 1000 liter op kunststof pallet met aftapkraan	1.2	1	1.16	1.39	63	1000	€ 330.00	[15]

Result		
Weight [kg/1000 L Fuel]	62.7	kg
Volume [L/ 1000 L Fuel]	1.4	m^3
Volume factor	39%	
Weight factor	6%	

Table C.5: Waterpumps

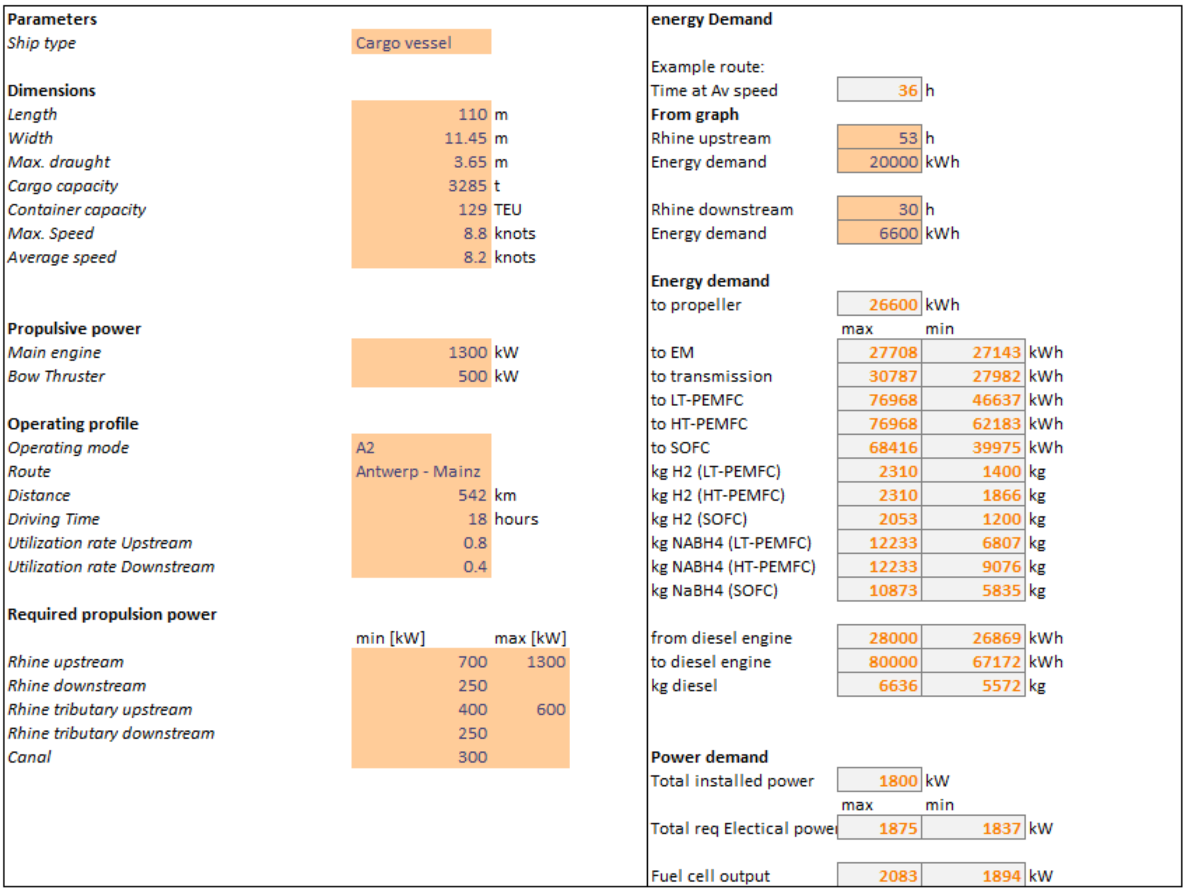
Name	**type**	**W [m]**	**D [m]**	**H [m]**	**V[m^3]**	**Weight [kg]**	**Flow Rate [L/min]**	**[l/s]**	**kg/l/s**	**m3/l/s**	**Power [kW]**	**Power [kW/l/s]**	**Pump Height [m]**	**Rotational speed (no load) [rpm]**	**cite**
Raider RD-PK60	Peripheral pump					5.05	35	0.58	8.66		0.37	0.63	35	2850	[51]
Raider RD-WP158	centrifugal pump					11.55	120	2.00	5.78		0.85	0.43	35	2900	[51]
Raider RD-2DK20	centrifugal pump					16.52	500	8.33	1.98		1.50	0.18	20	2850	[51]
Clarke BIP1000 1" Electrical Water pump	centrifugal pump	0.25	0.122	0.15	0.0046	5.2	40	0.67	7.80	0.007	0.38	0.57	35		[39]
Clarke CPE15A1 Industrial Self Priming Water Pump	centrifugal pump					14	325	5.42	2.58		0.75	0.14	16		[39]
JINTAI Q60	Peripheral pump	0.28	0.135	0.175	0.0066	5.5	36	0.60	9.17	0.011	0.37	0.62	36		[53]
JINTAI Q70	Peripheral pump	0.32	0.175	0.2	0.0112	9	46	0.77	11.74	0.015	0.55	0.72	60		[53]
JINTAI Q80	Peripheral pump	0.32	0.175	0.2	0.0112	10.5	50	0.83	12.60	0.013	0.75	0.90	72		[53]
Alfa Laval GM	centrifugal pump	0.307	0.171	0.305	0.0160	11	10	0.17	66.00	0.096	0.55	3.30	25		[66]

Results	min	max
Volume [m3/l/s UPW]	0.0069	0.0146
Weight [kg/l/s UPW]	1.98	12.60
power demand [kW/l/s]	0.14	3.30

D

Appendix D: Application cases

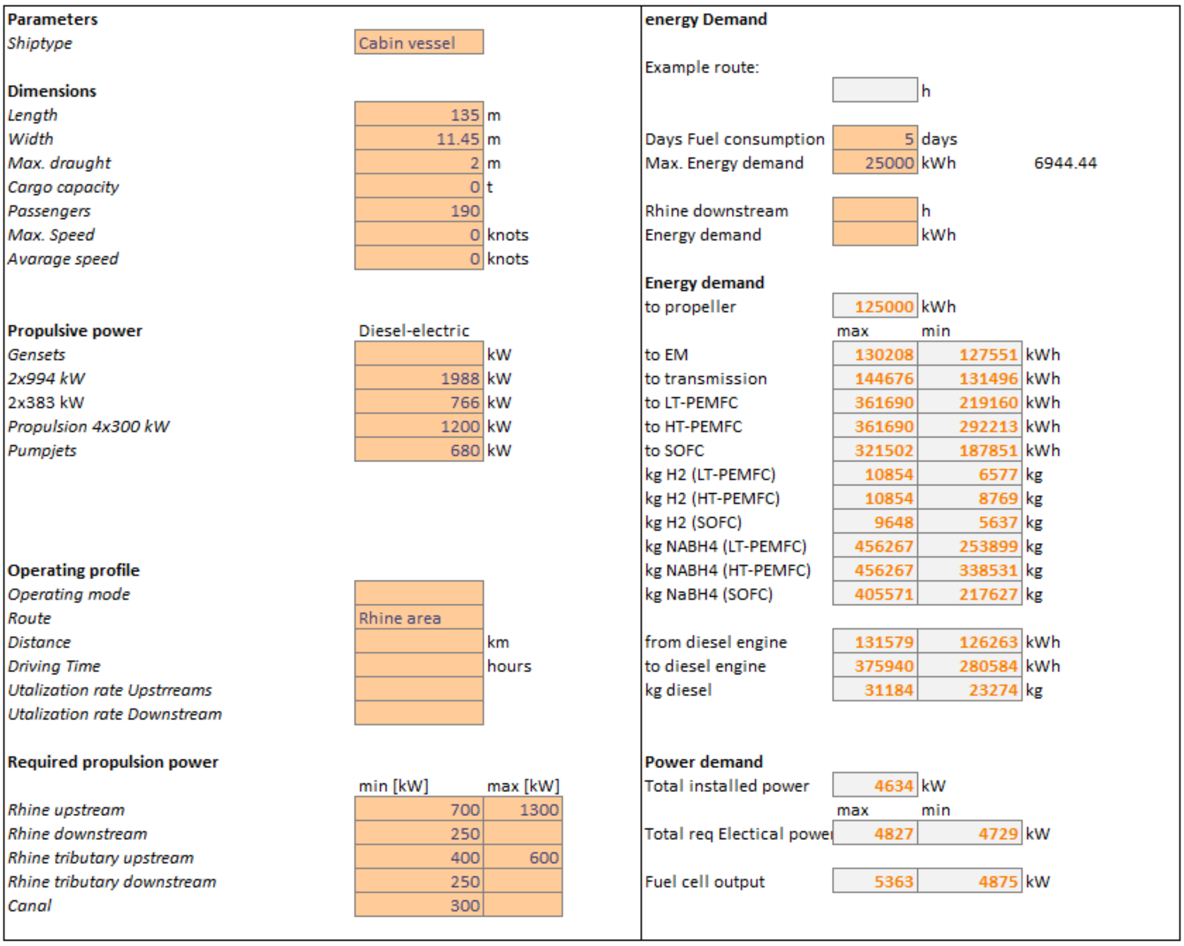
Table D.1: Parameters of a typical cargo vessel on the Rhine



Parameters		
Ship type	Cargo vessel	
Dimensions		
Length	110	m
Width	11.45	m
Max. draught	3.65	m
Cargo capacity	3285	t
Container capacity	129	TEU
Max. Speed	8.8	knots
Average speed	8.2	knots
Propulsive power		
Main engine	1300	kW
Bow Thruster	500	kW
Operating profile		
Operating mode	A2	
Route	Antwerp - Mainz	
Distance	542	km
Driving Time	18	hours
Utilization rate Upstream	0.8	
Utilization rate Downstream	0.4	
Required propulsion power		
	min [kW]	max [kW]
Rhine upstream	700	1300
Rhine downstream	250	
Rhine tributary upstream	400	600
Rhine tributary downstream	250	
Canal	300	

energy Demand			
Example route:			
Time at Av speed	36	h	
From graph			
Rhine upstream	53	h	
Energy demand	20000	kWh	
Rhine downstream	30	h	
Energy demand	6600	kWh	
Energy demand			
to propeller	26600	kWh	
	max	min	
to EM	27708	27143	kWh
to transmission	30787	27982	kWh
to LT-PEMFC	76968	46637	kWh
to HT-PEMFC	76968	62183	kWh
to SOFC	68416	39975	kWh
kg H2 (LT-PEMFC)	2310	1400	kg
kg H2 (HT-PEMFC)	2310	1866	kg
kg H2 (SOFC)	2053	1200	kg
kg NABH4 (LT-PEMFC)	12233	6807	kg
kg NABH4 (HT-PEMFC)	12233	9076	kg
kg NaBH4 (SOFC)	10873	5835	kg
from diesel engine	28000	26869	kWh
to diesel engine	80000	67172	kWh
kg diesel	6636	5572	kg
Power demand			
Total installed power	1800	kW	
	max	min	
Total req Electical powe	1875	1837	kW
Fuel cell output	2083	1894	kW

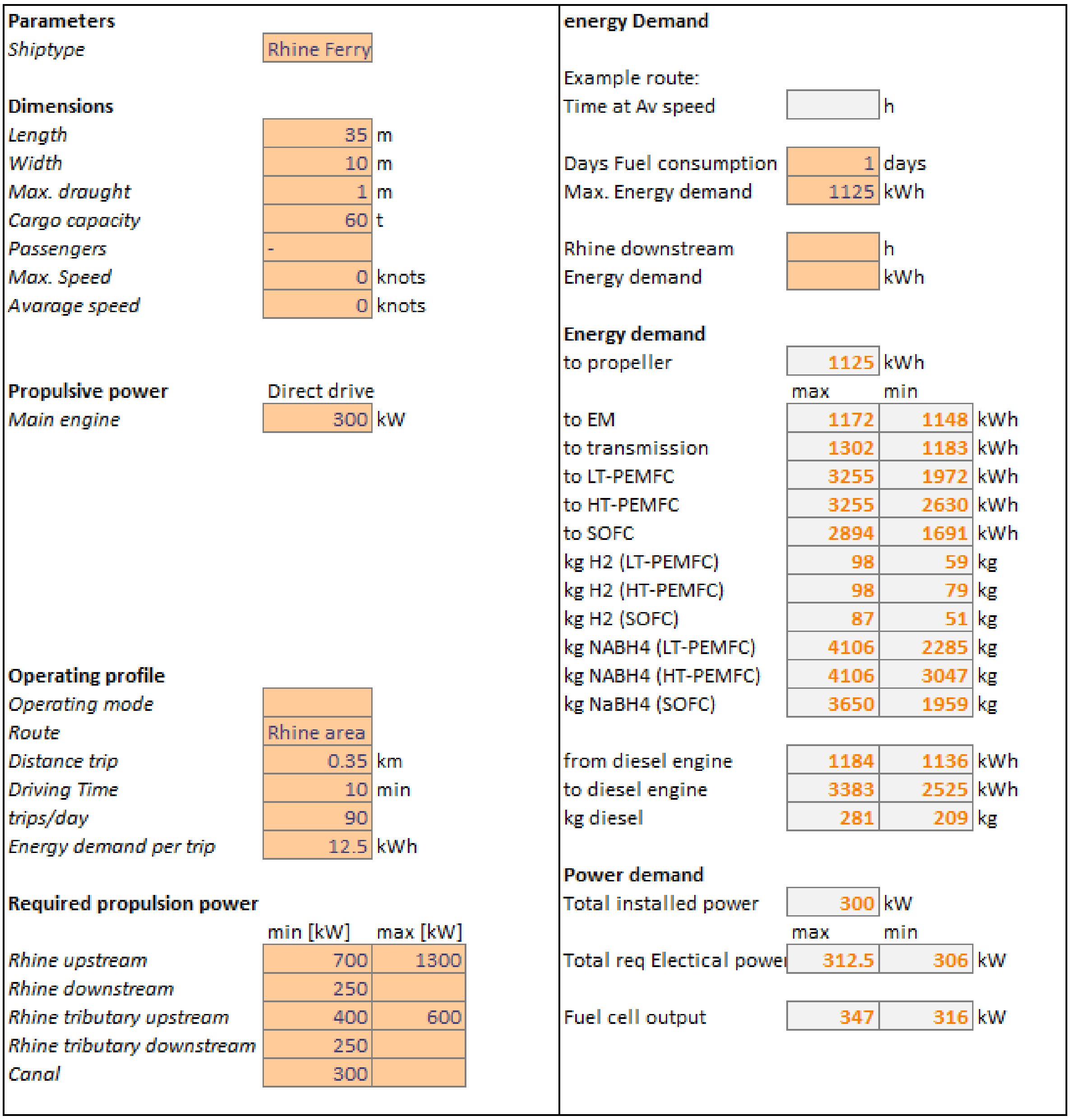
Table D.2: Parameters of a typical cabin vessel on the Rhine



Parameters		
Shiptype	Cabin vessel	
Dimensions		
Length	135	m
Width	11.45	m
Max. draught	2	m
Cargo capacity	0	t
Passengers	190	
Max. Speed	0	knots
Avarage speed	0	knots
Propulsive power	Diesel-electric	
Gensets		kW
2x994 kW	1988	kW
2x383 kW	766	kW
Propulsion 4x300 kW	1200	kW
Pumpjets	680	kW
Operating profile		
Operating mode		
Route	Rhine area	
Distance		km
Driving Time		hours
Utalization rate Upstreams		
Utalization rate Downstream		
Required propulsion power		
	min [kW]	max [kW]
Rhine upstream	700	1300
Rhine downstream	250	
Rhine tributary upstream	400	600
Rhine tributary downstream	250	
Canal	300	

energy Demand				
Example route:				
		h		
Days Fuel consumption	5	days		
Max. Energy demand	25000	kWh		6944.44
Rhine downstream		h		
Energy demand		kWh		
Energy demand				
to propeller	125000	kWh		
	max	min		
to EM	130208	127551	kWh	
to transmission	144676	131496	kWh	
to LT-PEMFC	361690	219160	kWh	
to HT-PEMFC	361690	292213	kWh	
to SOFC	321502	187851	kWh	
kg H2 (LT-PEMFC)	10854	6577	kg	
kg H2 (HT-PEMFC)	10854	8769	kg	
kg H2 (SOFC)	9648	5637	kg	
kg NABH4 (LT-PEMFC)	456267	253899	kg	
kg NABH4 (HT-PEMFC)	456267	338531	kg	
kg NaBH4 (SOFC)	405571	217627	kg	
from diesel engine	131579	126263	kWh	
to diesel engine	375940	280584	kWh	
kg diesel	31184	23274	kg	
Power demand				
Total installed power	4634	kW		
	max	min		
Total req Electical powe	4827	4729	kW	
Fuel cell output	5363	4875	kW	

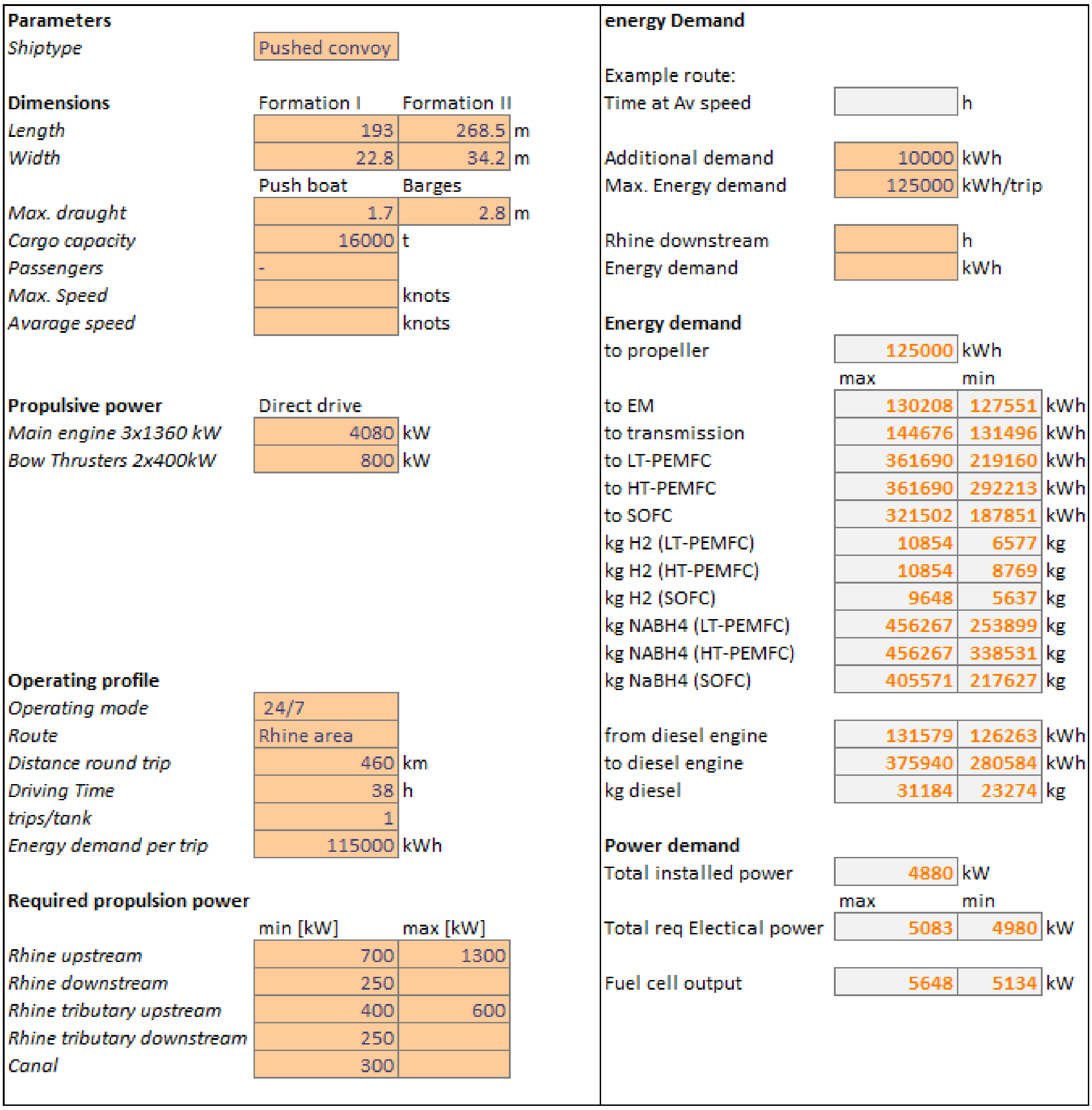
Table D.3: Parameters of a typical Rhine ferry



Parameters			
Shiptype	Rhine Ferry		
Dimensions			
Length	35	m	
Width	10	m	
Max. draught	1	m	
Cargo capacity	60	t	
Passengers	-		
Max. Speed	0	knots	
Avarage speed	0	knots	
Propulsive power	Direct drive		
Main engine	300	kW	
Operating profile			
Operating mode			
Route	Rhine area		
Distance trip	0.35	km	
Driving Time	10	min	
trips/day	90		
Energy demand per trip	12.5	kWh	
Required propulsion power			
	min [kW]	max [kW]	
Rhine upstream	700	1300	
Rhine downstream	250		
Rhine tributary upstream	400	600	
Rhine tributary downstream	250		
Canal	300		

energy Demand			
Example route:			
Time at Av speed		h	
Days Fuel consumption	1	days	
Max. Energy demand	1125	kWh	
Rhine downstream		h	
Energy demand		kWh	
Energy demand			
to propeller	1125	kWh	
	max	min	
to EM	1172	1148	kWh
to transmission	1302	1183	kWh
to LT-PEMFC	3255	1972	kWh
to HT-PEMFC	3255	2630	kWh
to SOFC	2894	1691	kWh
kg H2 (LT-PEMFC)	98	59	kg
kg H2 (HT-PEMFC)	98	79	kg
kg H2 (SOFC)	87	51	kg
kg NABH4 (LT-PEMFC)	4106	2285	kg
kg NABH4 (HT-PEMFC)	4106	3047	kg
kg NaBH4 (SOFC)	3650	1959	kg
from diesel engine	1184	1136	kWh
to diesel engine	3383	2525	kWh
kg diesel	281	209	kg
Power demand			
Total installed power	300	kW	
	max	min	
Total req Electical powe	312.5	306	kW
Fuel cell output	347	316	kW

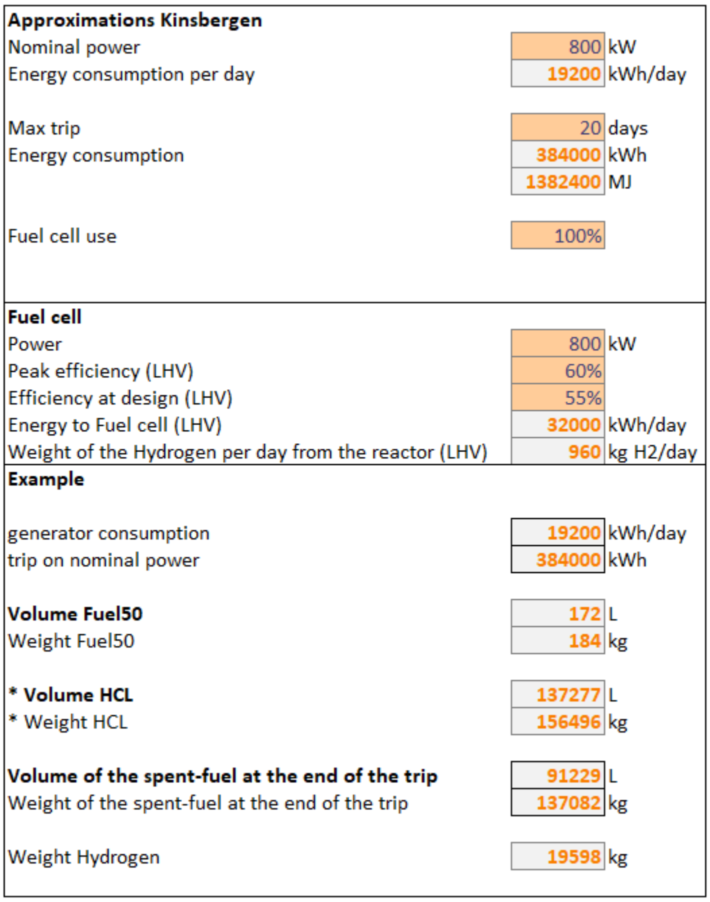
Table D.4: Parameters of a pushed convoy on the Rhine



Parameters			
Shiptype	Pushed convoy		
Dimensions	Formation I	Formation II	
Length	193	268.5	m
Width	22.8	34.2	m
	Push boat	Barges	
Max. draught	1.7	2.8	m
Cargo capacity	16000	t	
Passengers	-		
Max. Speed		knots	
Avarage speed		knots	
Propulsive power	Direct drive		
Main engine 3x1360 kW	4080	kW	
Bow Thrusters 2x400kW	800	kW	
Operating profile			
Operating mode	24/7		
Route	Rhine area		
Distance round trip	460	km	
Driving Time	38	h	
trips/tank	1		
Energy demand per trip	115000	kWh	
Required propulsion power			
	min [kW]	max [kW]	
Rhine upstream	700	1300	
Rhine downstream	250		
Rhine tributary upstream	400	600	
Rhine tributary downstream	250		
Canal	300		

energy Demand			
Example route:			
Time at Av speed		h	
Additional demand	10000	kWh	
Max. Energy demand	125000	kWh/trip	
Rhine downstream		h	
Energy demand		kWh	
Energy demand			
to propeller	125000	kWh	
	max	min	
to EM	130208	127551	kWh
to transmission	144676	131496	kWh
to LT-PEMFC	361690	219160	kWh
to HT-PEMFC	361690	292213	kWh
to SOFC	321502	187851	kWh
kg H2 (LT-PEMFC)	10854	6577	kg
kg H2 (HT-PEMFC)	10854	8769	kg
kg H2 (SOFC)	9648	5637	kg
kg NABH4 (LT-PEMFC)	456267	253899	kg
kg NABH4 (HT-PEMFC)	456267	338531	kg
kg NaBH4 (SOFC)	405571	217627	kg
from diesel engine	131579	126263	kWh
to diesel engine	375940	280584	kWh
kg diesel	31184	23274	kg
Power demand			
Total installed power	4880	kW	
	max	min	
Total req Electical power	5083	4980	kW
Fuel cell output	5648	5134	kW

Table D.5: Fuel volume and weight estimation on a marine trainings vessel



Approximations Kinsbergen		
Nominal power	800	kW
Energy consumption per day	19200	kWh/day
Max trip	20	days
Energy consumption	384000	kWh
	1382400	MJ
Fuel cell use	100%	
Fuel cell		
Power	800	kW
Peak efficiency (LHV)	60%	
Efficiency at design (LHV)	55%	
Energy to Fuel cell (LHV)	32000	kWh/day
Weight of the Hydrogen per day from the reactor (LHV)	960	kg H2/day
Example		
generator consumption	19200	kWh/day
trip on nominal power	384000	kWh
Volume Fuel50	172	L
Weight Fuel50	184	kg
* **Volume HCL**	137277	L
* Weight HCL	156496	kg
Volume of the spent-fuel at the end of the trip	91229	L
Weight of the spent-fuel at the end of the trip	137082	kg
Weight Hydrogen	19598	kg

E

Appendix E: Chemical cards

SODIUM TETRAHYDROBORATE Sodium borohydride	**ICSC: 1670** **October 2006**
CAS #: 16940-66-2 **UN #: 1426** **EINECS #: 241-004-4**	

	ACUTE HAZARDS	PREVENTION	FIRE FIGHTING
FIRE & EXPLOSION	Combustible. Risk of fire and explosion on contact with acids, alcohol, oxidizing agents or water.	NO open flames.	Use dry sand, dry powder. NO water. NO foam. NO carbon dioxide.

AVOID ALL CONTACT! IN ALL CASES CONSULT A DOCTOR!			
	SYMPTOMS	**PREVENTION**	**FIRST AID**
Inhalation	Burning sensation. Cough. Sore throat. Laboured breathing. Shortness of breath.	Use local exhaust or breathing protection.	Fresh air, rest. Refer immediately for medical attention.
Skin	Redness. Pain. Skin burns.	Protective gloves. Protective clothing.	First rinse with plenty of water for at least 15 minutes, then remove contaminated clothes and rinse again. Refer for medical attention .
Eyes	Redness. Pain. Severe deep burns.	Wear safety goggles or eye protection in combination with breathing protection.	Rinse with plenty of water for several minutes (remove contact lenses if easily possible). Refer immediately for medical attention.
Ingestion	Burning sensation in the throat and chest. Abdominal pain. Vomiting. Shock or collapse.	Do not eat, drink, or smoke during work.	Rinse mouth. Give one or two glasses of water to drink. Do NOT induce vomiting. Refer immediately for medical attention.

SPILLAGE DISPOSAL

Remove all ignition sources. Personal protection: chemical protection suit and particulate filter respirator adapted to the airborne concentration of the substance. Sweep spilled substance into covered dry, plastic containers. Carefully collect remainder. Then store and dispose of according to local regulations.

STORAGE

Dry. Well closed. Separated from strong acids, alcohols, powdered metals and water.

PACKAGING

CLASSIFICATION & LABELLING

According to UN GHS Criteria

DANGER

In contact with water releases flammable gases which may ignite spontaneously
Toxic if swallowed
Causes severe skin burns and eye damage

Transportation
UN Classification
UN Hazard Class: 4.3; UN Pack Group: I

International Labour Organization
World Health Organization

Prepared by an international group of experts on behalf of ILO and WHO, with the financial assistance of the European Commission.

European Commission

SODIUM TETRAHYDROBORATE	ICSC: 1670

PHYSICAL & CHEMICAL INFORMATION

Physical State; Appearance
WHITE CRYSTALLINE POWDER.

Physical dangers
No data.

Chemical dangers
Decomposes on heating and on contact with acids, powdered metals, water and moisture. This produces flammable/explosive gas (hydrogen - see ICSC 0001). The substance is a strong reducing agent. It reacts violently with oxidants. This generates fire and explosion hazard.

Formula: $NaBH_4$
Molecular mass: 37.8
Decomposes at >250°C
Density: 1.07 g/cm^3
Solubility in water, g/100ml at 25°C: 55
Auto-ignition temperature: ~220°C
Explosive limits, vol% in air: 3.02 - ?

EXPOSURE & HEALTH EFFECTS

Routes of exposure
Serious local effects by all routes of exposure.

Effects of short-term exposure
The substance is corrosive to the eyes, skin and respiratory tract. Corrosive on ingestion.

Inhalation risk
A harmful concentration of airborne particles can be reached quickly when dispersed.

Effects of long-term or repeated exposure

OCCUPATIONAL EXPOSURE LIMITS

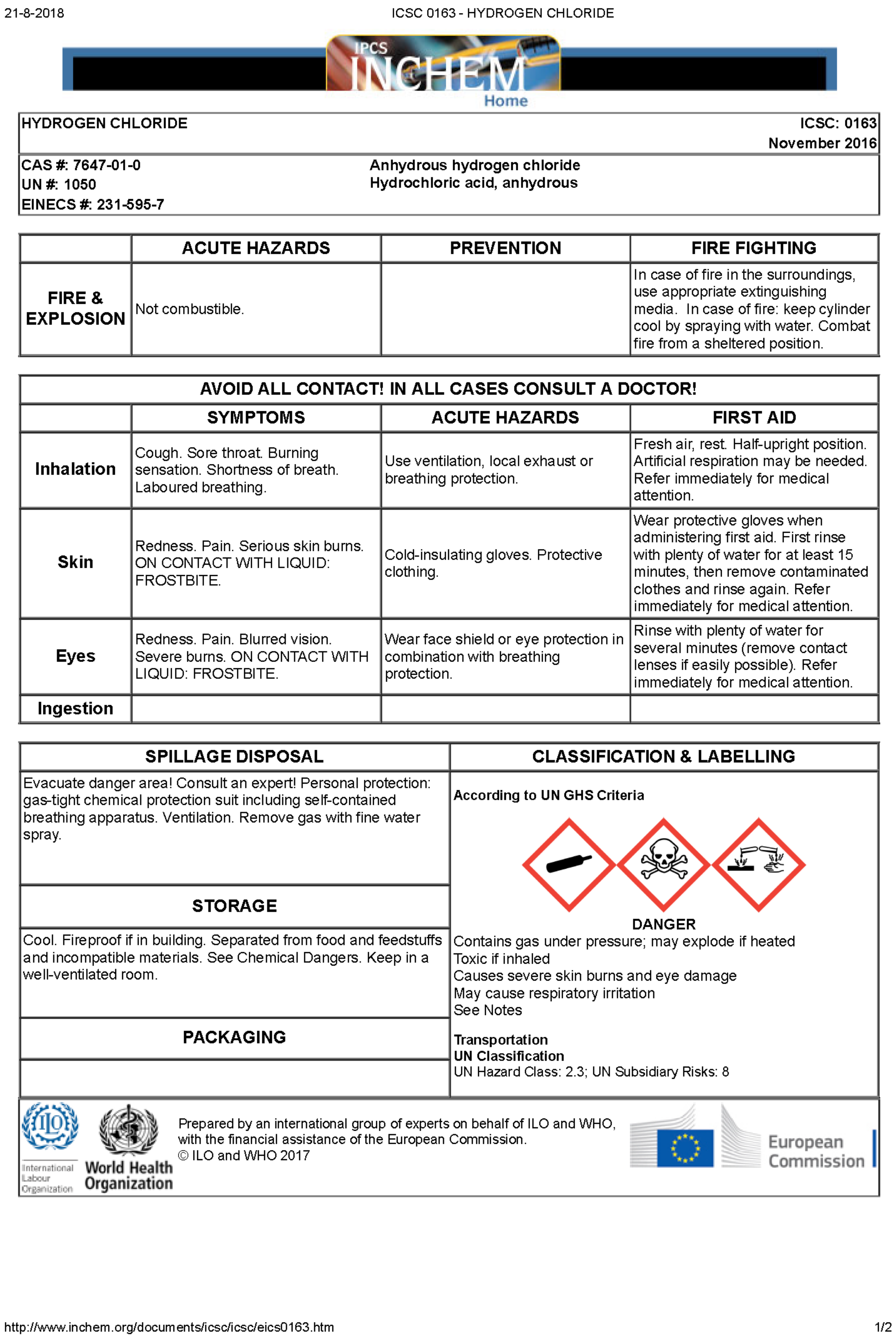
ENVIRONMENT

NOTES

Reacts violently with fire extinguishing agents such as water.

ADDITIONAL INFORMATION

EC Classification



21-8-2018 ICSC 0163 - HYDROGEN CHLORIDE

IPCS INCHEM
Home

HYDROGEN CHLORIDE	**ICSC: 0163** **November 2016**
CAS #: 7647-01-0 **UN #: 1050** **EINECS #: 231-595-7**	**Anhydrous hydrogen chloride** **Hydrochloric acid, anhydrous**

	ACUTE HAZARDS	PREVENTION	FIRE FIGHTING
FIRE & EXPLOSION	Not combustible.		In case of fire in the surroundings, use appropriate extinguishing media. In case of fire: keep cylinder cool by spraying with water. Combat fire from a sheltered position.

AVOID ALL CONTACT! IN ALL CASES CONSULT A DOCTOR!

	SYMPTOMS	ACUTE HAZARDS	FIRST AID
Inhalation	Cough. Sore throat. Burning sensation. Shortness of breath. Laboured breathing.	Use ventilation, local exhaust or breathing protection.	Fresh air, rest. Half-upright position. Artificial respiration may be needed. Refer immediately for medical attention.
Skin	Redness. Pain. Serious skin burns. ON CONTACT WITH LIQUID: FROSTBITE.	Cold-insulating gloves. Protective clothing.	Wear protective gloves when administering first aid. First rinse with plenty of water for at least 15 minutes, then remove contaminated clothes and rinse again. Refer immediately for medical attention.
Eyes	Redness. Pain. Blurred vision. Severe burns. ON CONTACT WITH LIQUID: FROSTBITE.	Wear face shield or eye protection in combination with breathing protection.	Rinse with plenty of water for several minutes (remove contact lenses if easily possible). Refer immediately for medical attention.
Ingestion			

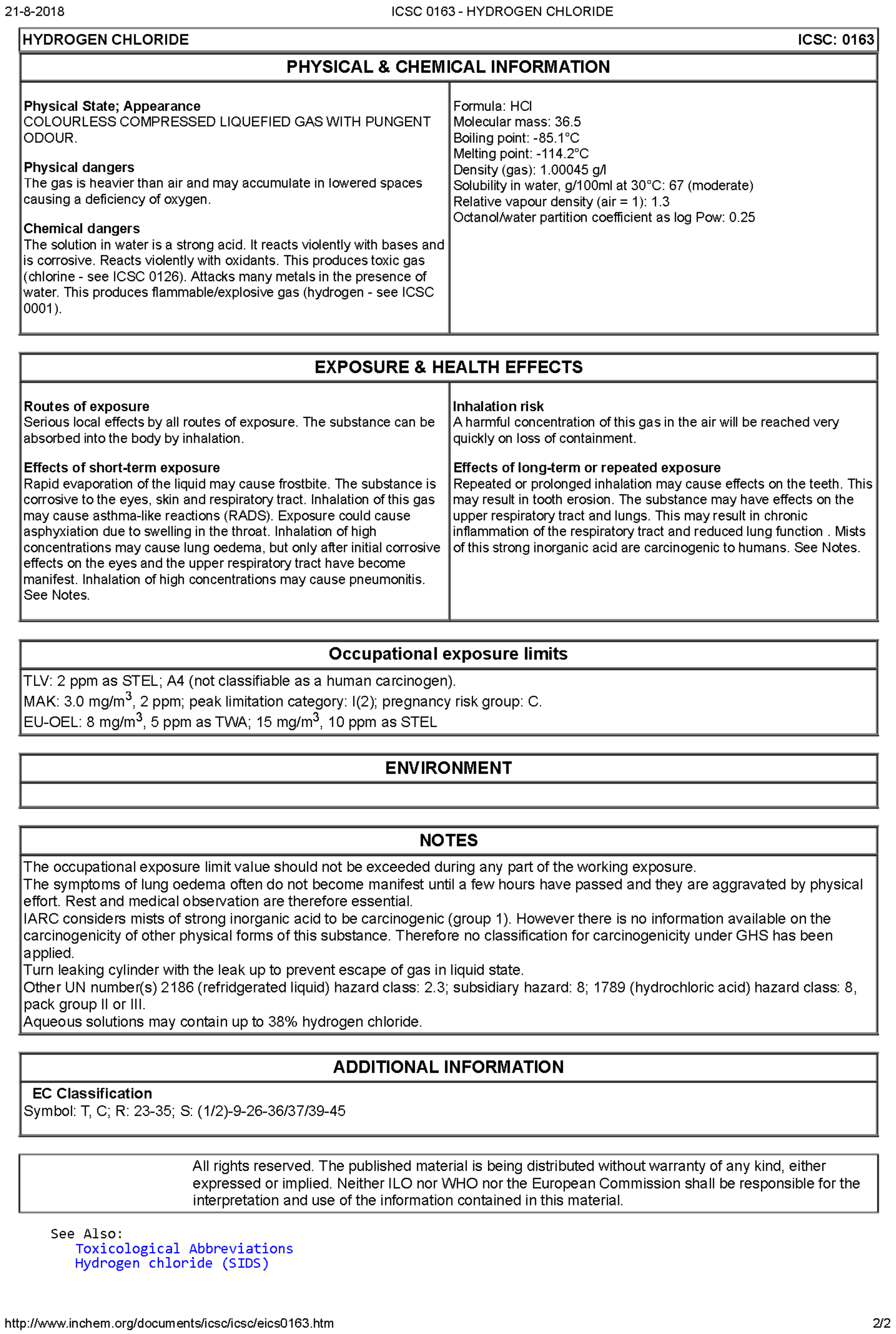
SPILLAGE DISPOSAL	CLASSIFICATION & LABELLING
Evacuate danger area! Consult an expert! Personal protection: gas-tight chemical protection suit including self-contained breathing apparatus. Ventilation. Remove gas with fine water spray.	**According to UN GHS Criteria** DANGER Contains gas under pressure; may explode if heated Toxic if inhaled Causes severe skin burns and eye damage May cause respiratory irritation See Notes **Transportation** **UN Classification** UN Hazard Class: 2.3; UN Subsidiary Risks: 8
STORAGE	
Cool. Fireproof if in building. Separated from food and feedstuffs and incompatible materials. See Chemical Dangers. Keep in a well-ventilated room.	
PACKAGING	

International Labour Organization World Health Organization

Prepared by an international group of experts on behalf of ILO and WHO, with the financial assistance of the European Commission.

European Commission

http://www.inchem.org/documents/icsc/icsc/eics0163.htm 1/2



HYDROGEN CHLORIDE **ICSC: 0163**

PHYSICAL & CHEMICAL INFORMATION

Physical State; Appearance
COLOURLESS COMPRESSED LIQUEFIED GAS WITH PUNGENT ODOUR.

Physical dangers
The gas is heavier than air and may accumulate in lowered spaces causing a deficiency of oxygen.

Chemical dangers
The solution in water is a strong acid. It reacts violently with bases and is corrosive. Reacts violently with oxidants. This produces toxic gas (chlorine - see ICSC 0126). Attacks many metals in the presence of water. This produces flammable/explosive gas (hydrogen - see ICSC 0001).

Formula: HCl
Molecular mass: 36.5
Boiling point: -85.1°C
Melting point: -114.2°C
Density (gas): 1.00045 g/l
Solubility in water, g/100ml at 30°C: 67 (moderate)
Relative vapour density (air = 1): 1.3
Octanol/water partition coefficient as log Pow: 0.25

EXPOSURE & HEALTH EFFECTS

Routes of exposure
Serious local effects by all routes of exposure. The substance can be absorbed into the body by inhalation.

Effects of short-term exposure
Rapid evaporation of the liquid may cause frostbite. The substance is corrosive to the eyes, skin and respiratory tract. Inhalation of this gas may cause asthma-like reactions (RADS). Exposure could cause asphyxiation due to swelling in the throat. Inhalation of high concentrations may cause lung oedema, but only after initial corrosive effects on the eyes and the upper respiratory tract have become manifest. Inhalation of high concentrations may cause pneumonitis. See Notes.

Inhalation risk
A harmful concentration of this gas in the air will be reached very quickly on loss of containment.

Effects of long-term or repeated exposure
Repeated or prolonged inhalation may cause effects on the teeth. This may result in tooth erosion. The substance may have effects on the upper respiratory tract and lungs. This may result in chronic inflammation of the respiratory tract and reduced lung function . Mists of this strong inorganic acid are carcinogenic to humans. See Notes.

Occupational exposure limits

TLV: 2 ppm as STEL; A4 (not classifiable as a human carcinogen).
MAK: 3.0 mg/m^3, 2 ppm; peak limitation category: I(2); pregnancy risk group: C.
EU-OEL: 8 mg/m^3, 5 ppm as TWA; 15 mg/m^3, 10 ppm as STEL

ENVIRONMENT

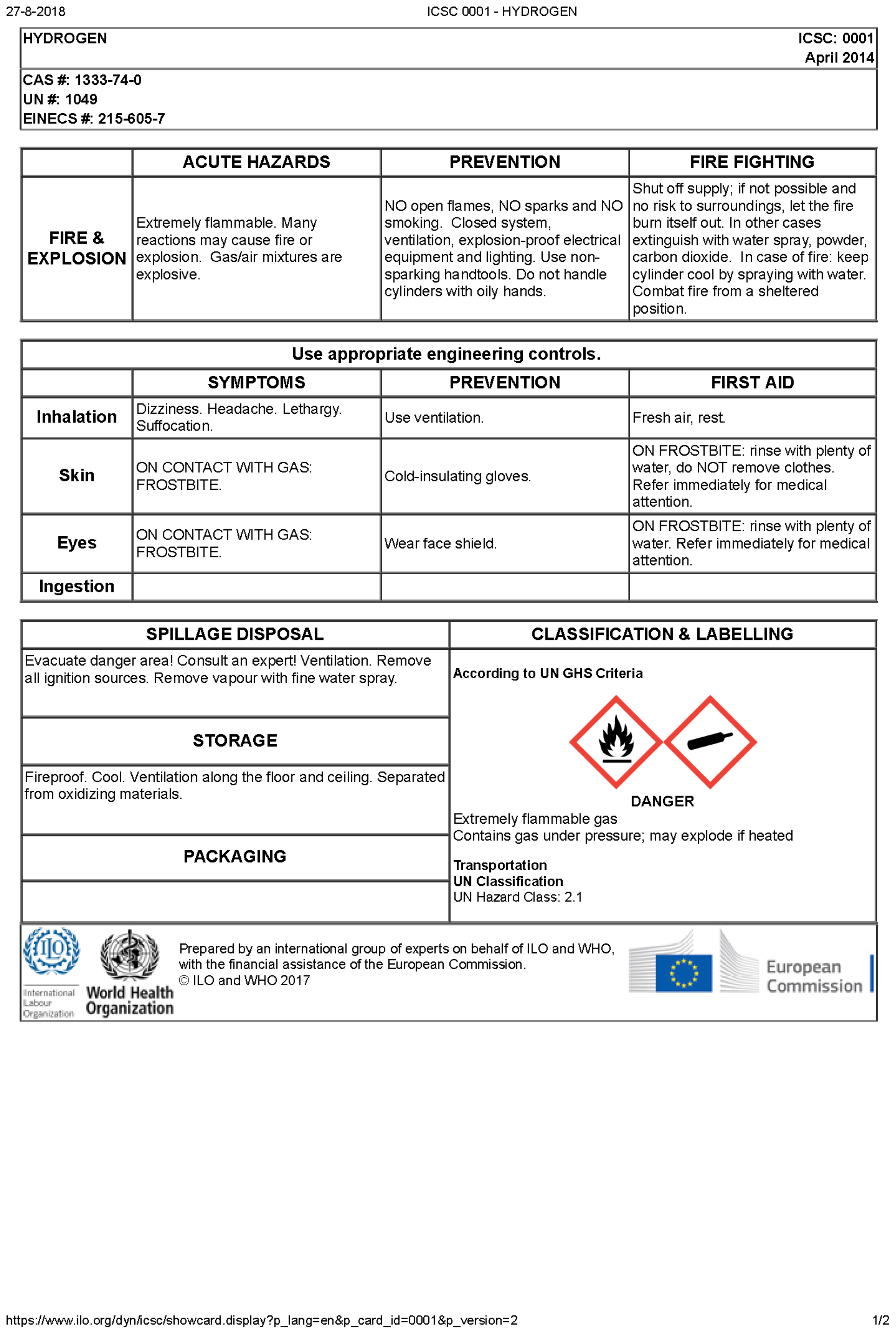
NOTES

The occupational exposure limit value should not be exceeded during any part of the working exposure.
The symptoms of lung oedema often do not become manifest until a few hours have passed and they are aggravated by physical effort. Rest and medical observation are therefore essential.
IARC considers mists of strong inorganic acid to be carcinogenic (group 1). However there is no information available on the carcinogenicity of other physical forms of this substance. Therefore no classification for carcinogenicity under GHS has been applied.
Turn leaking cylinder with the leak up to prevent escape of gas in liquid state.
Other UN number(s) 2186 (refridgerated liquid) hazard class: 2.3; subsidiary hazard: 8; 1789 (hydrochloric acid) hazard class: 8, pack group II or III.
Aqueous solutions may contain up to 38% hydrogen chloride.

ADDITIONAL INFORMATION

EC Classification
Symbol: T, C; R: 23-35; S: (1/2)-9-26-36/37/39-45

See Also:
Toxicological Abbreviations
Hydrogen chloride (SIDS)



27-8-2018 ICSC 0001 - HYDROGEN

HYDROGEN	**ICSC: 0001** **April 2014**
CAS #: 1333-74-0 **UN #: 1049** **EINECS #: 215-605-7**	

	ACUTE HAZARDS	PREVENTION	FIRE FIGHTING
FIRE & EXPLOSION	Extremely flammable. Many reactions may cause fire or explosion. Gas/air mixtures are explosive.	NO open flames, NO sparks and NO smoking. Closed system, ventilation, explosion-proof electrical equipment and lighting. Use non-sparking handtools. Do not handle cylinders with oily hands.	Shut off supply; if not possible and no risk to surroundings, let the fire burn itself out. In other cases extinguish with water spray, powder, carbon dioxide. In case of fire: keep cylinder cool by spraying with water. Combat fire from a sheltered position.

Use appropriate engineering controls.

	SYMPTOMS	PREVENTION	FIRST AID
Inhalation	Dizziness. Headache. Lethargy. Suffocation.	Use ventilation.	Fresh air, rest.
Skin	ON CONTACT WITH GAS: FROSTBITE.	Cold-insulating gloves.	ON FROSTBITE: rinse with plenty of water, do NOT remove clothes. Refer immediately for medical attention.
Eyes	ON CONTACT WITH GAS: FROSTBITE.	Wear face shield.	ON FROSTBITE: rinse with plenty of water. Refer immediately for medical attention.
Ingestion			

SPILLAGE DISPOSAL	CLASSIFICATION & LABELLING
Evacuate danger area! Consult an expert! Ventilation. Remove all ignition sources. Remove vapour with fine water spray.	**According to UN GHS Criteria** **DANGER** Extremely flammable gas Contains gas under pressure; may explode if heated **Transportation** **UN Classification** UN Hazard Class: 2.1
STORAGE	
Fireproof. Cool. Ventilation along the floor and ceiling. Separated from oxidizing materials.	
PACKAGING	

Prepared by an international group of experts on behalf of ILO and WHO, with the financial assistance of the European Commission.

https://www.ilo.org/dyn/icsc/showcard.display?p_lang=en&p_card_id=0001&p_version=2 1/2

HYDROGEN **ICSC: 0001**

PHYSICAL & CHEMICAL INFORMATION

Physical State; Appearance
ODOURLESS COLOURLESS COMPRESSED GAS.

Physical dangers
The gas mixes well with air, explosive mixtures are easily formed. The gas is lighter than air.

Chemical dangers
Heating may cause violent combustion or explosion. Reacts violently with halogens, oxidizing materials and greases. This generates fire and explosion hazard. Metal catalysts, such as platinum and nickel, greatly enhance these reactions.

Formula: H_2
Molecular mass: 2.0
Boiling point: -253°C
Melting point: -259°C
Relative vapour density (air = 1): 0.07
Flash point: Flammable gas
Auto-ignition temperature: 560°C
Explosive limits, vol% in air: 4-75
Vapour pressure, kPa at 25°C: 165320
Solubility in water, mg/l at 21°C: 1.62 (very poor)

EXPOSURE & HEALTH EFFECTS

Routes of exposure
Exposure mainly occurs via inhalation.

Effects of short-term exposure
Asphyxiation. See Notes. Exposure to cold gas could cause frostbite.

Inhalation risk
On loss of containment this substance can cause suffocation by lowering the oxygen content of the air in confined areas.

Effects of long-term or repeated exposure

OCCUPATIONAL EXPOSURE LIMITS

ENVIRONMENT

NOTES

High concentrations in the air cause a deficiency of oxygen with the risk of unconsciousness or death.
Check oxygen content before entering the area.
Measure hydrogen concentrations with suitable gas detector (a normal flammable gas detector is NOT suitable for the purpose).

ADDITIONAL INFORMATION

EC Classification
Symbol: F+; R: 12; S: (2)-9-16-33

F

Appendix F: Feasibility study CSA

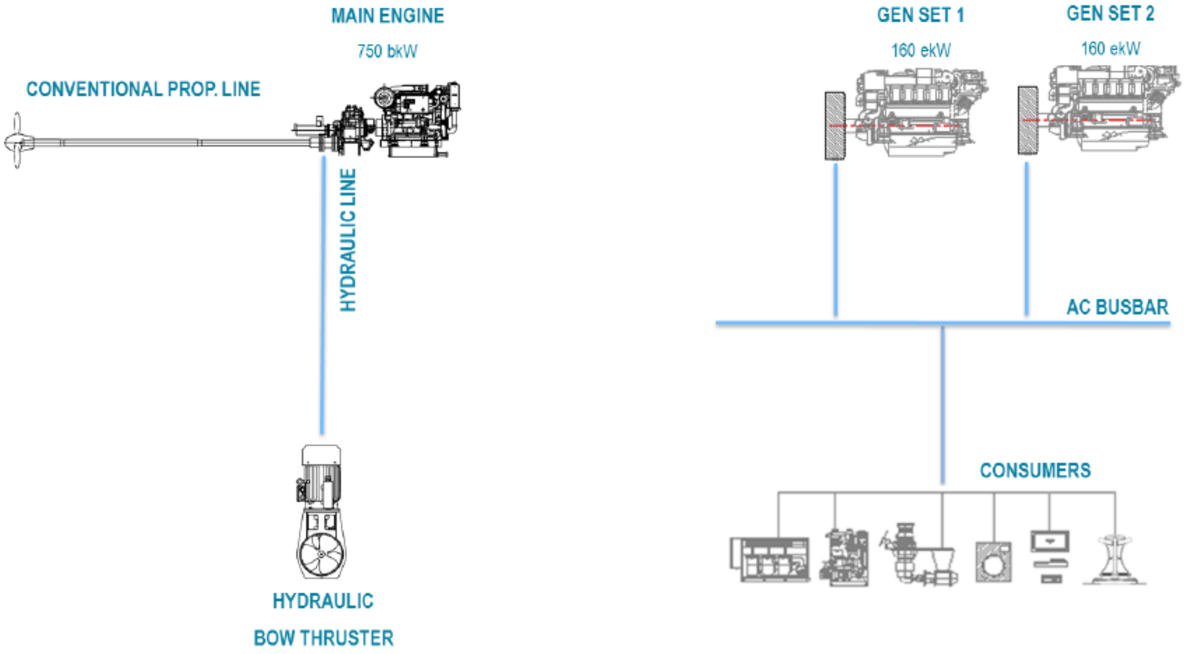


Figure F.1: Current configuration on-board of the CSA

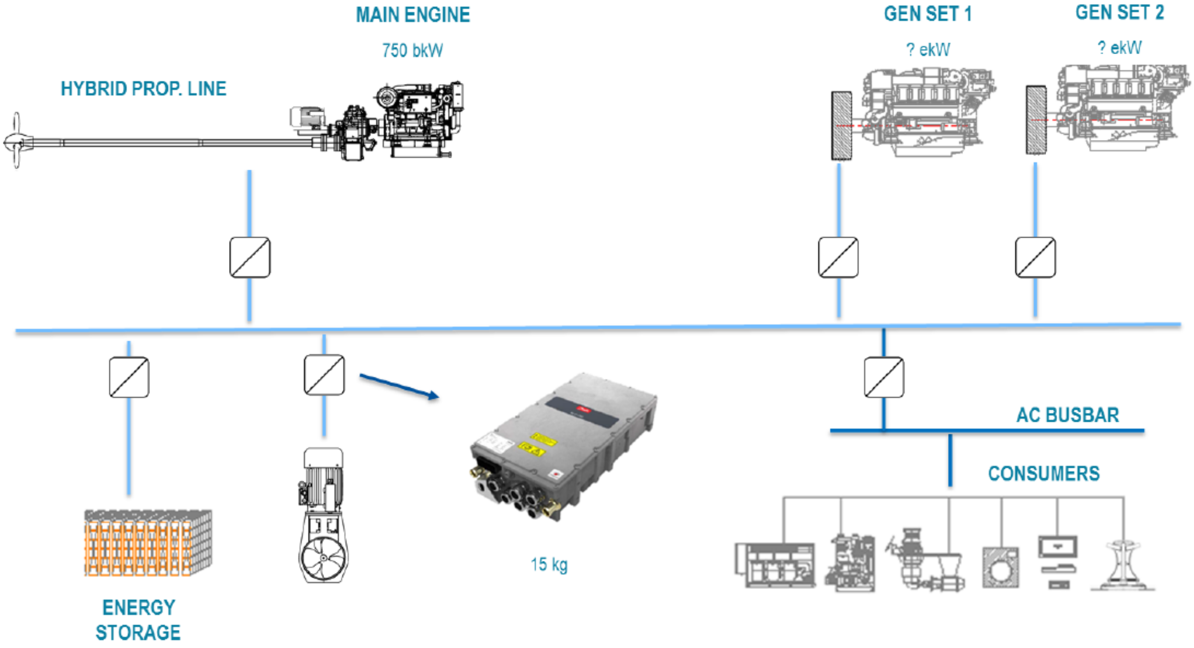


Figure F.2: Scenario 1 of the feasibility study on-board of the CSA

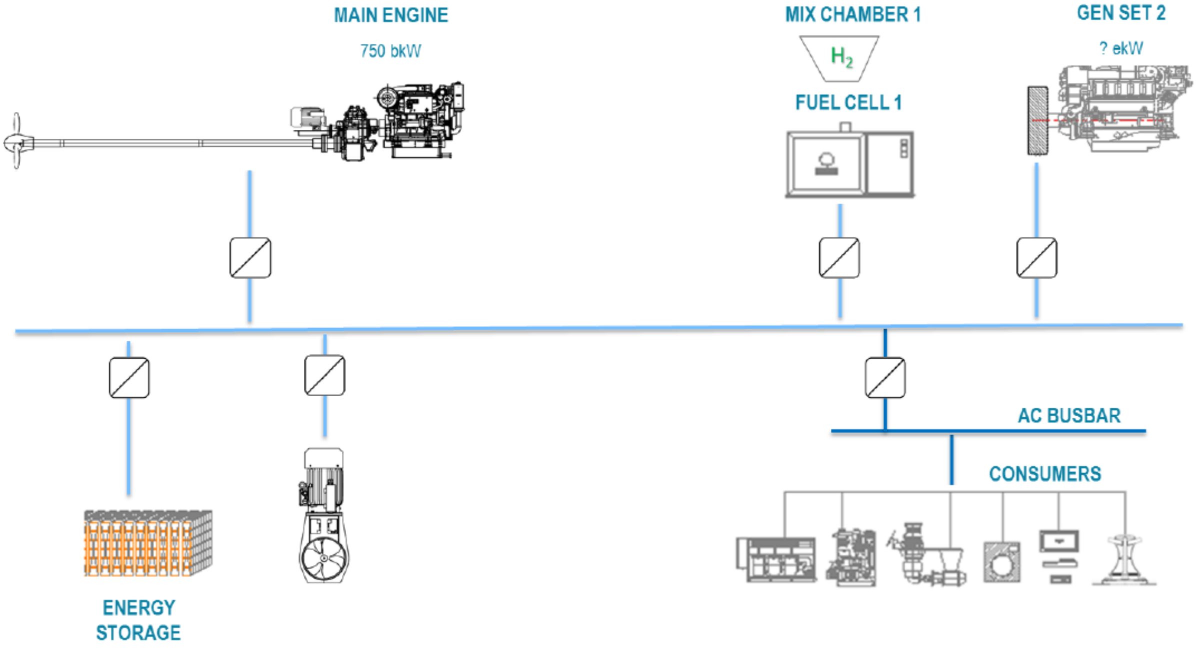


Figure F.3: Scenario 2 of the feasibility study on-board of the CSA

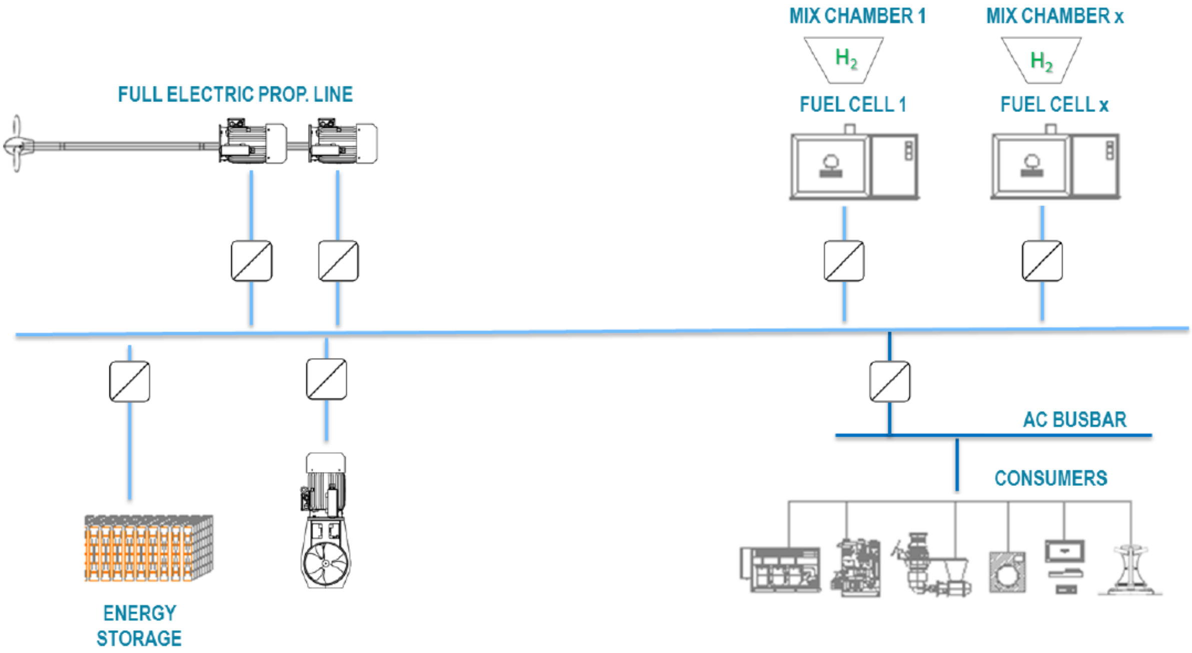


Figure F.4: Scenario 3 of the feasibility study on-board of the CSA

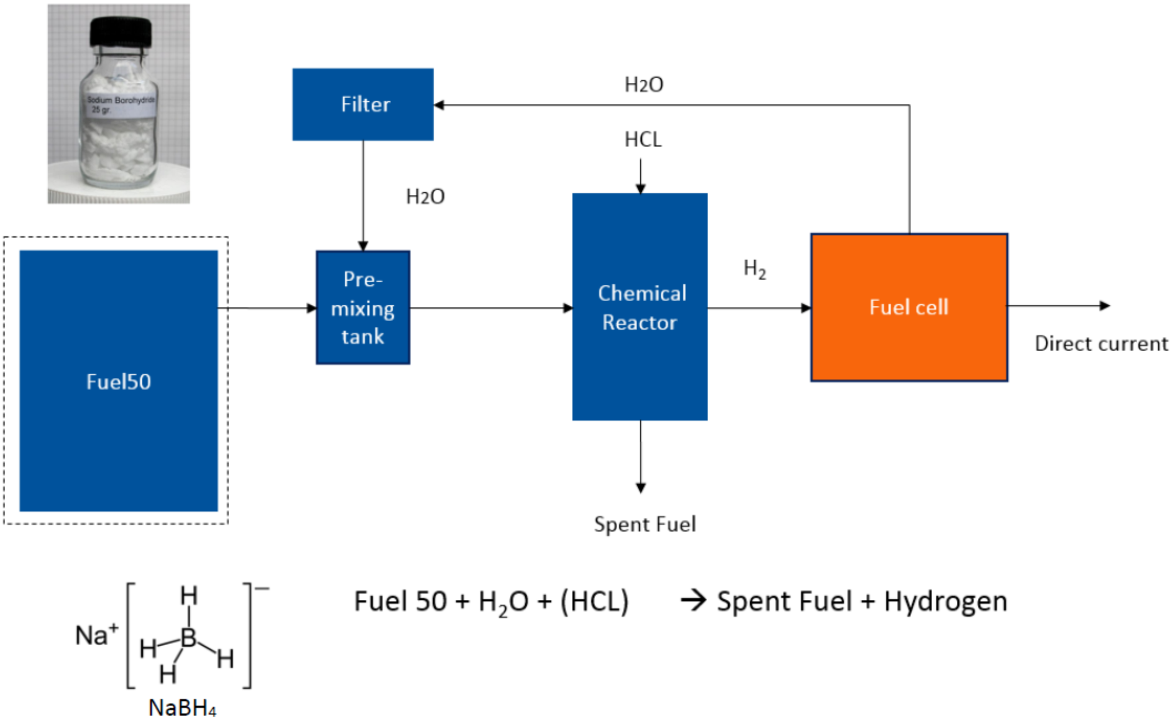
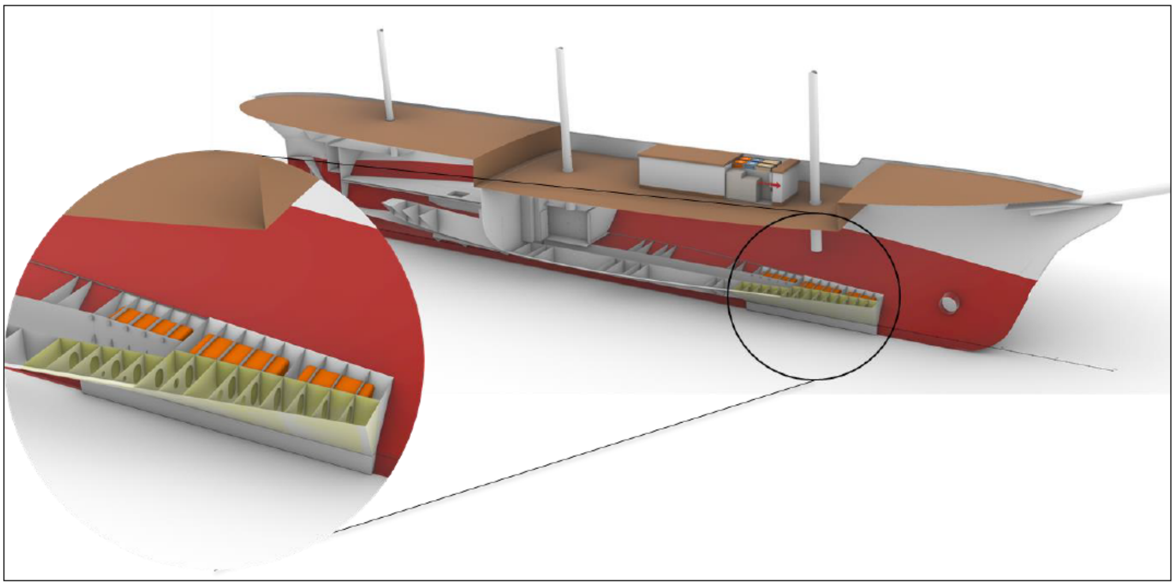
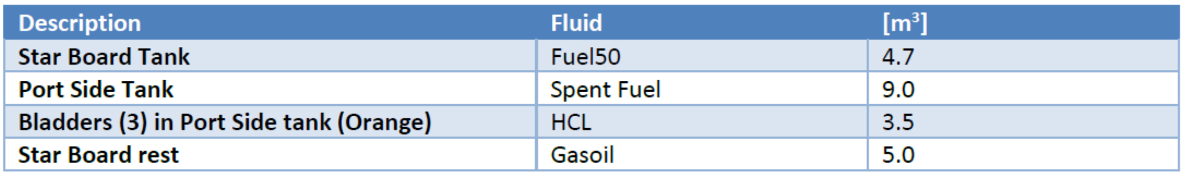


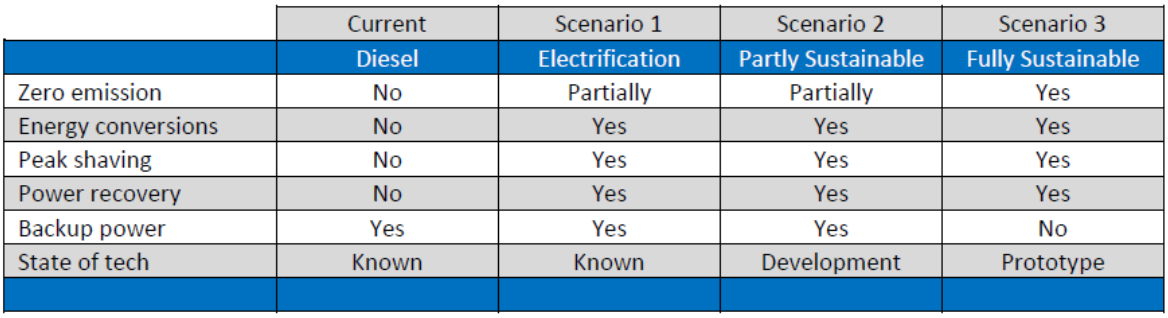
Figure F.5: Proposed hydrogen generation system for the feasibility study on-board of the CSA





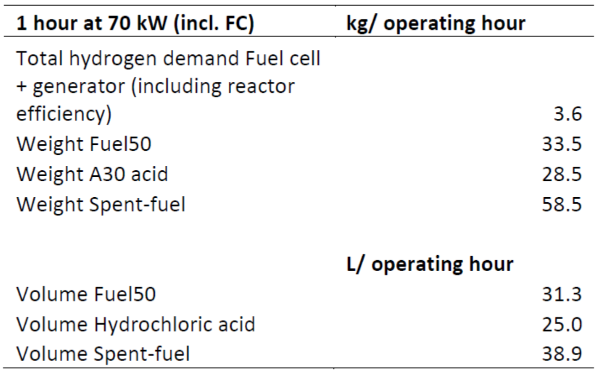
Description	Fluid	[m³]
Star Board Tank	Fuel50	4.7
Port Side Tank	Spent Fuel	9.0
Bladders (3) in Port Side tank (Orange)	HCL	3.5
Star Board rest	Gasoil	5.0

Figure F.6: Fuel volume calculation for 6 days hotel operation for the feasibility study on-board of the CSA



	Current	Scenario 1	Scenario 2	Scenario 3
	Diesel	Electrification	Partly Sustainable	Fully Sustainable
Zero emission	No	Partially	Partially	Yes
Energy conversions	No	Yes	Yes	Yes
Peak shaving	No	Yes	Yes	Yes
Power recovery	No	Yes	Yes	Yes
Backup power	Yes	Yes	Yes	No
State of tech	Known	Known	Development	Prototype

Figure F.7: Scenario overview of the feasibility study on-board of the CSA



1 hour at 70 kW (incl. FC)	**kg/ operating hour**
Total hydrogen demand Fuel cell + generator (including reactor efficiency)	3.6
Weight Fuel50	33.5
Weight A30 acid	28.5
Weight Spent-fuel	58.5
	L/ operating hour
Volume Fuel50	31.3
Volume Hydrochloric acid	25.0
Volume Spent-fuel	38.9

Figure F.8: Fuel volumes needed on an average load of 70 kW, a Fuel cell efficiency of 60% and a mix chamber hydrogen generation efficiency of 98%

G

Appendix G: Simulink model

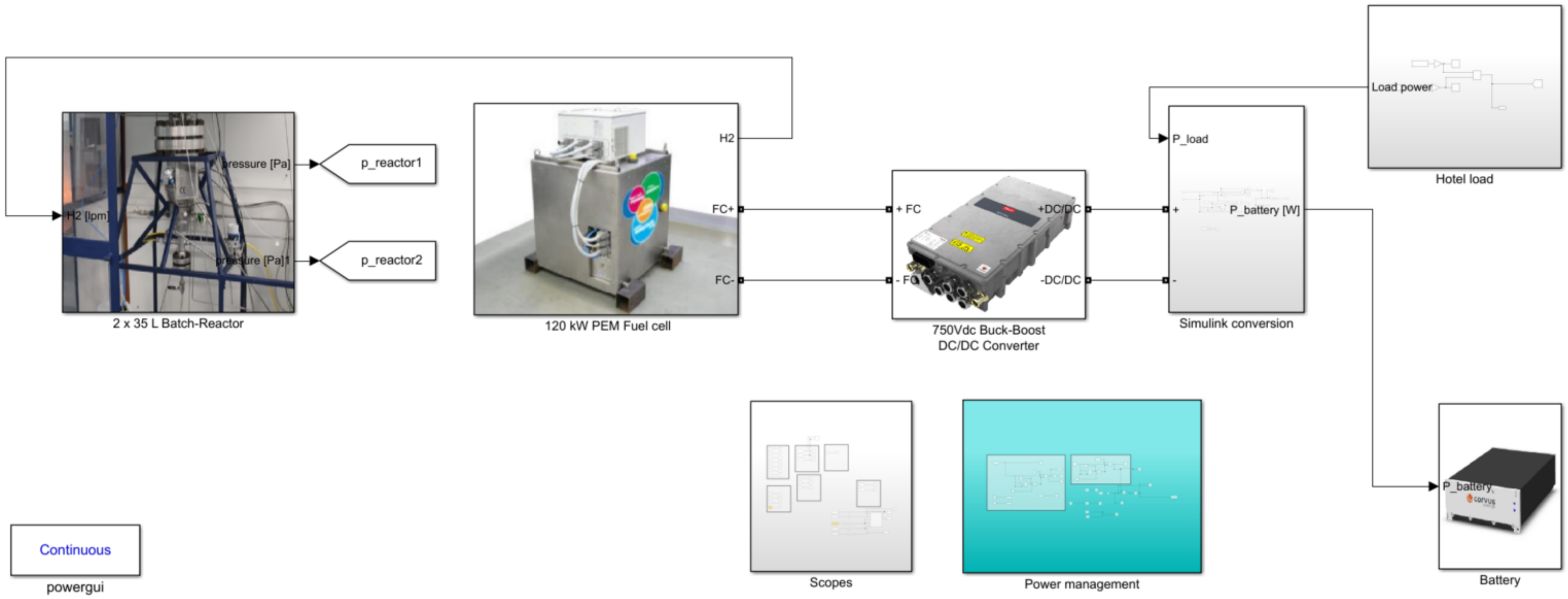


Figure G.1: Simulation model of the CSA

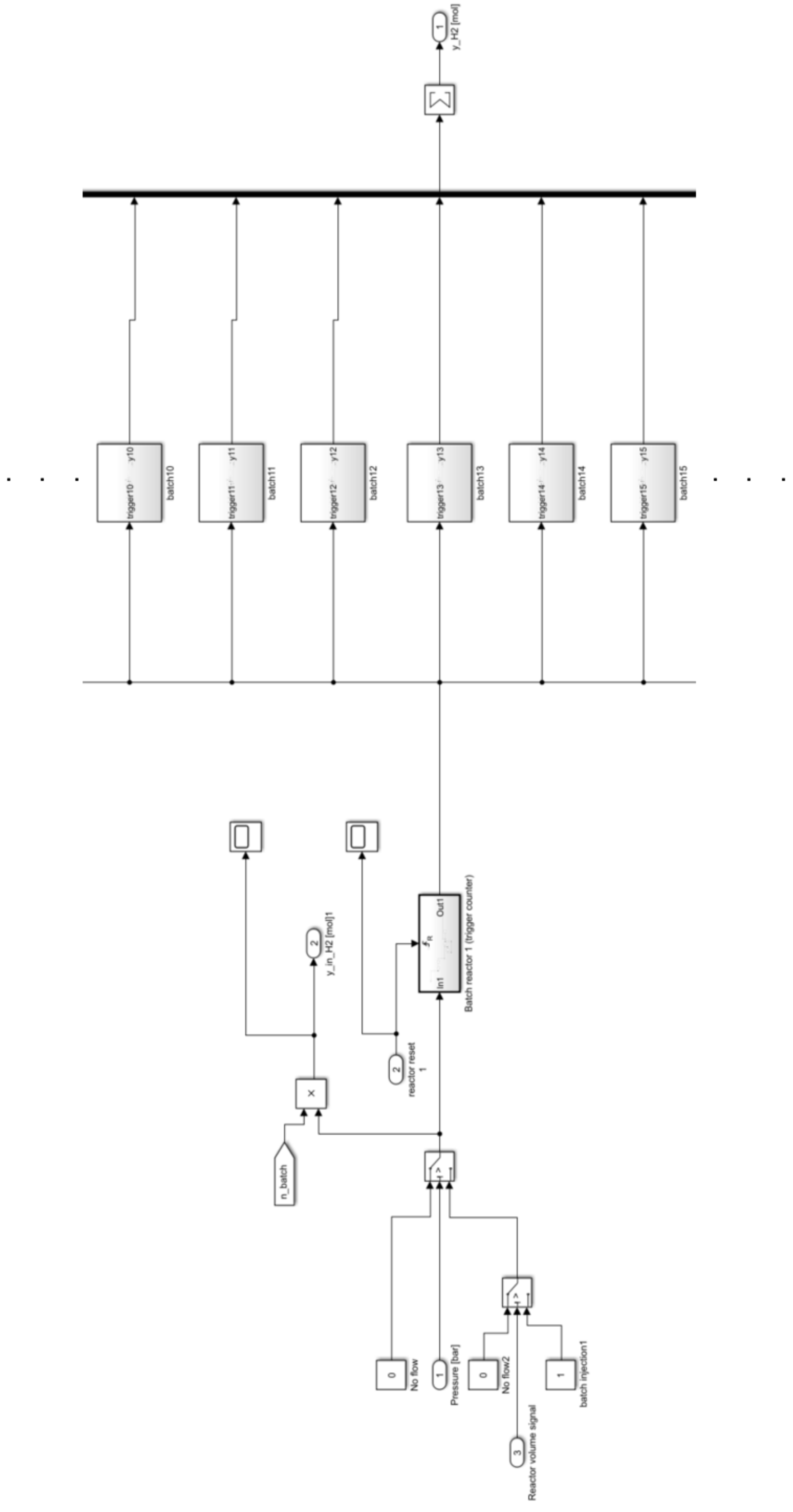


Figure G.2: Reactor injection control system

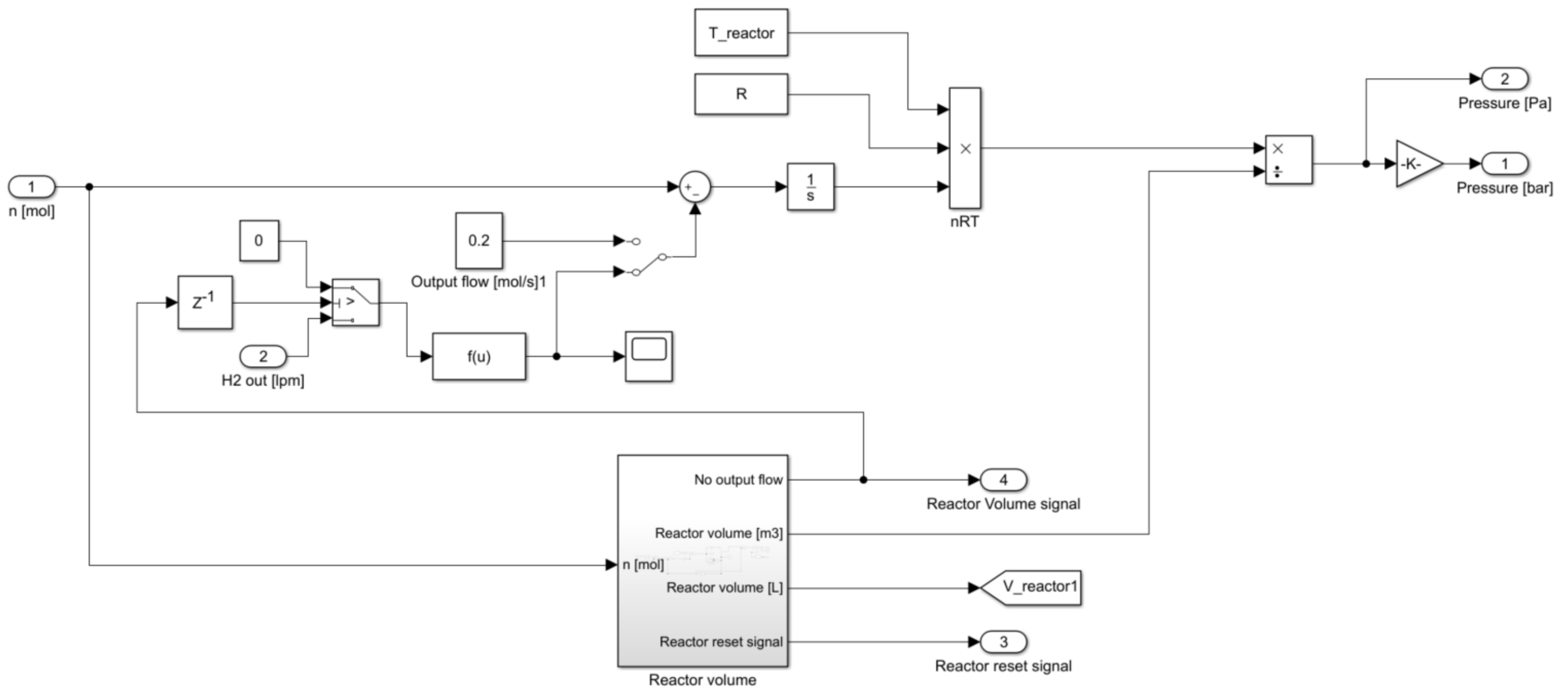


Figure G.3: Hydrogen buffer according to the ideal gas law

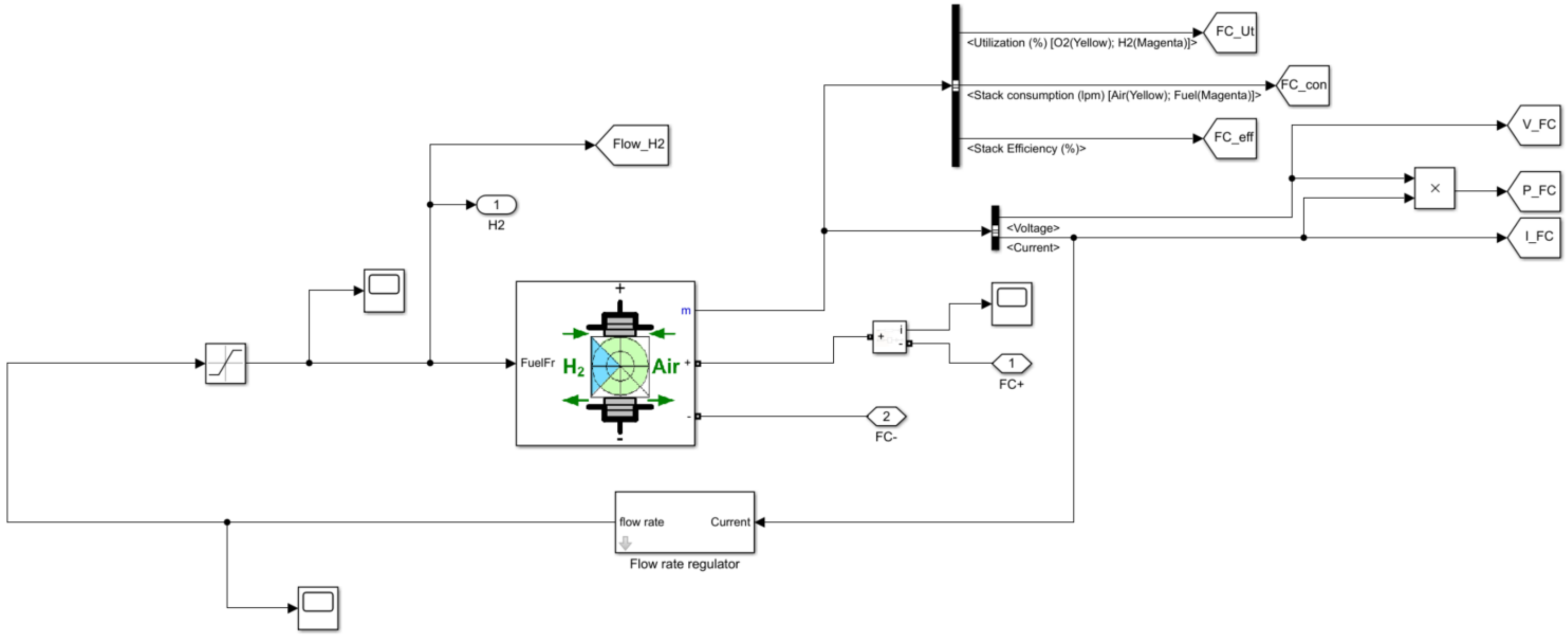


Figure G.4: Fuel cell model and fuel rate limiter