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Safe and effective application of ammonia as a marine fuel



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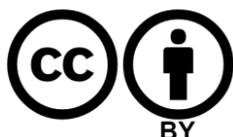
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Thesis for the degree of M.Sc. in Marine Technology in the specialisation of Marine Engineering

Safe and effective application of ammonia as a marine fuel

By



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Performed at

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SUMMARY

To achieve significant reduction in greenhouse gas emissions in shipping and enable ship owners to phase out fossil fuels entirely, renewable fuels, such as ammonia, play a crucial role. Ammonia is considered a balanced solution in terms of volumetric energy density and renewable synthetic production cost compared to other renewable fuels. However, many questions still need to be answered to determine if ammonia as a fuel for ships is a feasible option.

Therefore, the purpose of this project is to investigate how ammonia can be applied safely and effectively as a marine fuel. An ammonia carrier will be used to study the concept of using ammonia as a marine fuel. For this project the following options for ammonia fuel power generation are studied: the steam turbine, gas turbine, internal combustion engine (ICE) (both compression ignition (CI) and spark ignition (SI)) and fuel cells (both proton exchange membrane (PEMFC), alkaline (AFC) and solid oxide fuel cells (SOFC)). All options are found to be feasible onshore but only the internal combustion engine (using ammonia hydrogen mixtures) and all three fuel cells are considered feasible for marine applications.

Reviewing all options covering ICE, PEMFC, AFC and SOFC for marine applications the ICE has high efficiency and is sufficiently practical. The SOFC scores better in efficiency than the ICE but lacks power density, load response capability and is still too expensive. The ICE is second in efficiency and therefore more efficient than the PEMFC and the AFC (in case these are operated close to maximum power). Furthermore, the ICE is less expensive, more robust with acceptable power density and load response. Based on the comparison the ICE is currently selected as best option for this project. Comparing the ammonia ICE option with the conventional fossil fuelled ICE option the technical performance is similar on power density, load response, part load performance and system efficiency. However, the conventional option has significantly more harmful emissions. Studying the cost based on equal range the ammonia powered option is clearly more expensive, about 3.2 times the expenses of the conventional option. This follows from a basic cost scenario of 850 euro per ton ammonia and 500 euro per ton low sulphur 0.5% HFO. Looking into future scenarios the ammonia powered option can be in similar cost range as the conventional option. This is the case when using 400 euro per ton ammonia, based on low electricity cost, combined with either a 500 euro per ton HFO with 100 euro per ton CO₂ taxation or 811 euro per ton HFO without CO₂ taxation.

The main risks of ammonia are the toxicity and environmental impact. Ammonia is a gas at atmospheric conditions and highly toxic. Therefore, with storing and handling ammonia adequate means are required to limit the likelihood and effect of exposure to humans and the environment. Ammonia is also a flammable gas though it is relatively hard to ignite compared to conventional fuels (hence the need for hydrogen addition in the ICE). Considering the toxicity as ammonia can be lethal to humans at 2,700 ppm when exposed for a duration of 10 minutes. The lower flammability limit of ammonia is 15% which is equal to 150,000 ppm. Therefore, the flammability risks of ammonia are relatively low compared to the toxicity risks.

Reflecting on the risk assessment the main specific risks of using ammonia as a marine fuel are ammonia exposure to humans and the environment. In addition, in the fuel supply system considered the flammability risks of hydrogen, obtained from cracked ammonia, is present. To safely handle ammonia (and hydrogen) as a fuel, spaces containing fuel lines should be equipped with ammonia (and hydrogen) detection combined with ventilation. Furthermore, in case of leakages remote operated shut-off valves should be installed to isolate the leakage and limit its impact. In line with this mitigation, redundancy in the fuel supply line should be arranged to ensure sufficient fuel supply for continuous operation in case part of the fuel supply is shut-off. In addition, in case of a blackout the main remote

operated isolation valves should be installed with a fail close so when there is a loss of power the valves close automatically. As ammonia exposure to humans and the environment should be limited as much as possible, fuel lines should be routed with a sufficient distance from the shell, for example B/5 from the side. Where possible, fuel lines should be located in separate unmanned spaces. Where this is impossible, for example in the engine room, double-walled piping with pressure transmitters should be applied.

The main ship design consequences of the mitigations are on the arrangement due to the required separate spaces for the redundant fuel supply lines covering fuel trunks and fuel treatment rooms. Furthermore, the ventilation of the spaces containing fuel supply lines also require space for the intake and exhaust of air. The requirement of routing with sufficient distance from the side also impacts the effective use of available space of the vessel. All these factors increase the cost, especially the redundancy requirement. Therefore, implementation of 2 x 50% system capacity instead of 2 x 100% is considered to be important to limit these additional costs.

This project based the performance comparison on literature research and preliminary design calculations. The ammonia ICE option is selected to be the best solution for this project. Therefore, it is recommended to further investigate combustion of ammonia hydrogen mixtures in marine engines to obtain a more accurate view on performance like efficiency, load response, NOx emissions, fuel slip and several other performance criteria as a function of ammonia hydrogen mixture composition.

To realise ammonia as a marine fuel a step wise implementation could accelerate the application of ammonia as a marine fuel with in the first stage ammonia with marine diesel in an (CI) ICE. The second stage is an ICE using ammonia hydrogen mixtures followed by the third and final stage an SOFC using ammonia. Looking further into the first step, using ammonia with diesel in an (CI) ICE offers several benefits. This combination enables operators to significantly reduce harmful emissions while maintaining the reliability of a conventional marine engine. Furthermore, the ammonia fuel system will be less expensive as redundancy of ammonia fuel supply is not required when using redundant diesel fuel supply. Therefore, it is recommended to further investigate the technical feasibility of marine ICEs using ammonia and marine diesel as main fuel.

As fuel cell technology is still undergoing a lot of development it is recommended to maintain an accurate view on the technical and economic performance. Fuel cells might not power vessels today, but with its implementation ongoing in cars, buses, light trains and submarines they could become feasible for vessels for main power generation in the future. The SOFC seems particularly interesting as it can reach high efficiencies and is capable of handling multiple fuel types. Furthermore, the first application of fuel cells seems most preferable in ships which already have fuel-electric configurations. Therefore, it is recommended to further investigate the application of fuel cells in vessels, especially the SOFC and vessels which already have fuel-electric configurations.

The ammonia fuel system is based on the assumption that there is zero leakage in normal operational conditions. In practice this is not completely valid. Therefore, further analysis is considered to be required without the zero leakage assumption to continue the development. This should be further investigated and could be done with for example a quantitative analysis.

As an ammonia carrier is used for the ammonia fuel system the main issue of ammonia fuel storage is not addressed, as it was covered by existing regulations for transporting ammonia as cargo. Therefore, it is recommended to further investigate ammonia fuel storage so it can be applied on other ship types as well.

Overall, it can be stated that this research is a valuable first step towards the application of ammonia as a marine fuel. Yet a lot of additional research is still required to explore its full potential and feasibility.

ACKNOWLEDGEMENTS

For several years I have been fascinated by renewable fuels. Renewable fuels play a key role in both energy storage of renewable energy and eliminating greenhouse gas emissions. Each type of renewable fuel, like hydrogen, ammonia and methanol, have their own advantages and challenges. Considering aspects like ship type, local infrastructure, operational profile, importance of fuel cost versus (volumetric) energy density I believe multiple solutions will serve future needs coexisting next to each other. Ammonia is one of the potential renewable fuels. Therefore, it was with great pleasure to realise my master thesis, started in September 2018, investigating ammonia as a renewable fuel for the maritime industry.

First of all, I would like to thank all my colleagues at C-Job Naval Architects for their interest and support. Especially, my supervisors Peter Lankreijer and Wim Zindler. They are a great and unique duo with an impeccable taste for mechanical engineering including internal combustion engines covering both CI and SI. Their knowledge and experience were a valuable addition to the supervision and support of this project. In addition, I would also like to thank Tim Vlaar for sharing his insights in the application of natural gas fuel systems which were an important part of realising the ammonia fuel system. Furthermore, I am grateful for the efforts of Charlotte Mackenbach for additional review of my report and marketing activities of this project.

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TAKK FOR ALLT



Artist Impressions Ammonia Carrier, made by N. de Vries

Table of contents

Summary	4
Acknowledgements	6
List of Tables	11
List of Figures	12
Abbreviations	13
1 Introduction	14
2 Renewable Fuels	15
2.1 Energy Saving vs Energy Storage	15
2.2 Boundary Conditions	15
2.3 Renewable Fuel Options	17
2.4 Conclusion	18
3 Onshore Technical Feasibility of Ammonia Power Generation Options	19
3.1 Ammonia Combustion	19
3.2 Steam Turbine	19
3.3 Gas Turbine	20
3.4 Internal Combustion Engine	22
3.5 Fuel Cell	23
3.6 Conclusion	25
4 Marine Technical Feasibility of Ammonia Power Generation Options	26
4.1 Ship Type	26
4.2 Steam Turbine	27
4.3 Gas Turbine	27
4.4 Internal Combustion Engine	27
4.5 Fuel Cell	28
4.6 Conclusion	29
5 Marine Performance of Ammonia Power Generation Options	30
5.1 Performance Indicators	30
5.2 Internal Combustion Engine	32
5.3 PEMFC	41
5.4 AFC	47
5.5 SOFC	51

5.6	Comparison of Options.....	55
5.7	Conclusion	56
6	Ammonia Performance Comparison with Conventional Power Generation	57
6.1	Conventional Option	57
6.2	General Comparison.....	60
6.3	Cost Scenario Comparisons	61
6.4	Conclusion	65
6.5	Recommendations.....	65
6.6	Outlook.....	65
7	General Ammonia Safety.....	67
7.1	Hazards of Ammonia	67
7.2	Existing Safety Measures.....	68
7.3	Rules and Regulations	68
7.4	Ammonia in the Nitrogen Cycle	70
7.5	Risk Levels.....	71
8	General Hydrogen Safety	74
8.1	Hazards of Hydrogen	74
8.2	Risk levels	74
9	Risk Assessment Methodology.....	76
9.1	Risk Identification	76
9.2	Risk Analysis.....	76
9.3	Risk Assessment	76
9.4	Risk Mitigation.....	78
9.5	Work Flow Example.....	78
10	Ammonia as Marine Fuel Risk Assessment	80
10.1	Technical Basis System Diagram.....	80
10.2	Risk Assessment 1.....	82
10.3	Reflection on Result of Risk Assessment 1	86
10.4	Risk Assessment 2.....	86
10.5	Conclusion	88
10.6	Recommendations.....	89
11	Conclusion and Recommendations	90

11.1	Conclusion	90
11.2	Recommendations.....	92
	Bibliography.....	95

LIST OF TABLES

Table 2-1: Required otherwise unproductive land for biomass to supply the maritime industry.....	16
Table 2-2: Comparison of renewable fuel options.....	17
Table 4-1: Ammonia carrier type & selected size.....	26
Table 4-2: Ammonia carrier main particulars.....	26
Table 5-1: Design condition and distribution, ICE option.....	32
Table 5-2: Stoichiometric combustion comparing: Ammonia, Hydrogen and Methane (white columns chemical properties, blue columns comparison of equal energy content)	34
Table 5-3: Small scale ammonia lab test engines.....	34
Table 5-4: ICE efficiency clarification, ammonia hydrogen mixture translated in pure ammonia consumption.....	38
Table 5-5: Assumed ammonia hydrogen mixture, ICE option.....	38
Table 5-6: Δ CAPEX, ICE option.....	40
Table 5-7: Δ OPEX, ICE option	40
Table 5-8: Design condition and distribution, PEMFC option	41
Table 5-9: PEMFC efficiency clarification, hydrogen translated in ammonia consumption	45
Table 5-10: Δ CAPEX, PEMFC option	46
Table 5-11: Δ OPEX, PEMFC option	46
Table 5-12: Design condition and distribution, AFC option	47
Table 5-13: Δ CAPEX, AFC option	50
Table 5-14: Δ OPEX, AFC option	50
Table 5-15: Design condition and distribution, SOFC option	51
Table 5-16: Δ CAPEX, SOFC option	54
Table 5-17: Δ OPEX, SOFC option	54
Table 5-18: Comparison of options, Part 1.....	55
Table 5-19: Comparison of options, Part 2.....	55
Table 6-1: Design condition and distribution, Conventional option	57
Table 6-2: Harmful emissions Conventional option	58
Table 6-3: Δ CAPEX, Conventional option	59
Table 6-4: Δ OPEX, Conventional option	60
Table 6-5: Comparison with Conventional option, Part 1	60
Table 6-6: Comparison with Conventional option, Part 2.....	60
Table 6-7: Influence boil-off comparison with conventional option.....	64
Table 7-1: Hazard statements comparison of ammonia with other fuels	67
Table 7-2: Summary of minimum requirements, Ammonia, 2014 IGC Code, Chapter 19.....	69
Table 7-3: Fraction of chemical species of ammonia present with change in pH (at 25°C).....	71
Table 7-4: Acute Exposure Guideline Levels (AEG): Ammonia	72
Table 8-1: Hazard statements comparison of hydrogen with other fuels	74
Table 9-1: Risk matrix, People, Assets and Environment combined	77
Table 9-2: Part I: Risk assessment work flow methodology example: Identification, Analysis and Assessment.....	78
Table 9-3: Part II: Risk assessment work flow methodology example: Mitigation	78
Table 10-1: Design parameters NH3 fuel system diagram.....	80
Table 10-2: Original risk rating results risk assessment 1	83
Table 10-3: Final risk rating results risk assessment 1	84
Table 10-4: Risk rating results risk assessment 2	88

LIST OF FIGURES

Figure 2-1: Sustainable cycle for renewable fuels (examples: Hydrogen, Ammonia and Methanol) ...	15
Figure 3-1: Ammonia power generation: Overview	19
Figure 3-2: Ammonia power generation: Selection of onshore technically feasible options	25
Figure 4-1: Ammonia power generation: Selection of marine technically feasible options	29
Figure 5-1: System design ICE option	33
Figure 5-2: System design PEMFC option	43
Figure 5-3: System design AFC option	48
Figure 5-4: System design SOFC option	52
Figure 5-5: Cost comparison of options	55
Figure 5-6: Ammonia power generation: Selection of marine performance options	56
Figure 6-1: System design Conventional option	58
Figure 6-2: Cost scenario 1 comparison ICE (NH ₃) vs Conventional	61
Figure 6-3: Cost scenario 2 comparison ICE (NH ₃) vs Conventional	61
Figure 6-4: Cost scenario 3 comparison ICE (NH ₃) vs Conventional	62
Figure 6-5: Cost scenario 4 comparison ICE (NH ₃) vs Conventional	62
Figure 6-6: Cost scenario 4 comparison ICE (NH ₃) vs Conventional, CO ₂ tax translated in HFO price ..	63
Figure 6-7: ΔOPEX distribution per ship size (Scenario 4: ICE (NH ₃) with 400 €/ton NH ₃)	64
Figure 6-8: Renewable fuel implementation timeline	66
Figure 6-9: Ammonia implementation timeline	66
Figure 7-1: Simplified scheme of NH ₃ /NH ₄ ⁺ cycling in the marine boundary and ocean surface layers. Exchange processes of NH ₄ ⁺ across the ocean/sediment interface are not shown. (NH ₄ ⁺) _p stands for particulate NH ₄ ⁺ (NH ₄ ⁺ aerosol), DON stands for dissolved organic nitrogen, PhyPl and ZooPl stand for Phytoplankton and Zooplankton respectively, and Bac stands for bacteria. Dashed arrows depict uptake/assimilation and release/excretion. Small letters in italics represent physical, chemical, and biological processes: a, atmospheric transport processes; b, uptake and release in clouds; c, gas-to-particle conversion; d, gas exchange; e, wet and/or dry deposition; f, nitrogen fixation; g, photochemical decomposition, h, nitrification; j, decomposition. The scheme is copied from [86]. ..	71

ABBREVIATIONS

NH ₃	Ammonia
AC	Alternating Current
AEGL	Acute Exposure Guideline Levels
AFC	Alkaline Fuel Cell
B/5	Moulded Breath of the Vessel divided by 5
CI	Compression Ignition
CFR	Cooperative Fuel Research
CO ₂	Carbon Dioxide
CPP	Controllable Pitch Propeller
CR	Compression Ratio
DC	Direct Current
EPA	Environmental Protection Agency
FPP	Fixed Pitch Propeller
GHG	Greenhouse Gas
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
HCCI	Homogeneous Charge Compression Ignition
HFO	Heavy Fuel Oil
ICE	Internal Combustion Engine
IBC	International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk
IGC	International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
IGF	International Code of Safety for Ships Using Gases or Other Low-Flashpoint Fuels
IMAREST	The Institute of Marine Engineering, Science and Technology
IMO	International Maritime Organization
LNG	Liquid Natural Gas
LPG	Liquid Petrol Gas
MGO	Marine Gas Oil
NO _x	Nitrogen Oxides
ODS	Ozone-Depleting Substance
SCR	Selective Catalytic Reduction
SDS	Safety Data Sheet
SI	Spark Ignition
SNCR	Selective Non Catalytic Reduction
SOFC	Solid Oxide Fuel Cell
SO _x	Sulphur Oxides
PEMFC	Proton Exchange Membrane Fuel Cell
PGS	Publication series on Dangerous Substances
PM	Particulate Matter
PTO	Power Take Off
VOC	Volatile Organic Compound
ΔCAPEX	Capital Expenditures
ΔOPEX	Operational Expenditures
ΔTCO	Total Cost of Ownership

1 INTRODUCTION

To achieve significant reduction in greenhouse gas emissions in shipping and enable ship owners to phase out fossil fuels entirely, renewable fuels, such as ammonia, play a crucial role. Ammonia is considered a balanced solution in terms of volumetric energy density and renewable synthetic production cost compared to other renewable fuels. However, many questions still need to be answered to determine if ammonia as a fuel for ships is a feasible option.

Therefore, the purpose of this project is to investigate how ammonia can be applied safely and effectively as a marine fuel. An ammonia carrier will be used to study the concept of using ammonia as a marine fuel. To study effective use of ammonia as a marine fuel the following options for power generation are investigated: the steam turbine, gas turbine, internal combustion engine (both compression and spark ignition) and fuel cells (both proton exchange membrane, alkaline and solid oxide fuel cells). The results of effective use of ammonia as a marine fuel are used to develop an ammonia fuel system diagram. This diagram is studied by means of a qualitative risk assessment to gain insight in safety of using ammonia as a marine fuel.

To further elaborate on the aim of this project the research questions are given below:

Main: How can ammonia be applied safely and effectively as a marine fuel?

Sub-1: What is the potential of ammonia as a fuel in a sustainable future with respect to storage and production?

Sub-2: What is the technical feasibility of ammonia power generation onshore?

Sub-3: What is the technical feasibility of ammonia power generation for marine applications?

Sub-4: What is the performance of ammonia power generation for marine applications?

Sub-5: How does conventional power generation compare with ammonia power generation for marine applications?

Sub-6: What are the general properties of ammonia in consideration of risk & safety, and how to cope with them?

Sub-7: What risks are identified when using ammonia as a marine fuel?

Sub-8: What means are required to reduce the identified risks to an acceptable level, and how do they affect the design?

This report is set out as follows. Chapter 2 defines the basic fundamentals of what a renewable fuel is and why ammonia is selected for this project. In chapter 3 the onshore technical feasibility of each ammonia power generation option is studied. Chapter 4 looks into the marine technical feasibility accordingly and comes to a selection which is used in chapter 5 to study the marine performance. The conclusion of chapter 5 provides a final selection which is compared to the conventional option in Chapter 6. Chapter 7 and 8 elaborate on general ammonia and hydrogen safety respectively. In chapter 9 the risk assessment methodology is explained and applied in chapter 10 on the ammonia fuel system diagram. Chapter 11 provides the main conclusions and recommendations of this project.

2 RENEWABLE FUELS

In this chapter the boundary conditions of renewable fuels will be explained. Furthermore, the potential of ammonia will be identified in comparison with other options with respect to storage and production. All data presented in this chapter has been obtained by research efforts prior to the start of the thesis. However, the academic reporting has been done after the kick-off of the thesis project.

2.1 Energy Saving vs Energy Storage

To reduce the impact on our climate and achieve the goals set up by the International Maritime Organization (IMO) regarding Greenhouse Gas (GHG) emissions ship owners can look both into means of energy saving and alternative in energy storage. Using conventional fossil fuels and means of energy saving alone will not enable the maritime industry to fully eliminate harmful emissions which is the ultimate goal set up by IMO regarding GHG emissions. Therefore, alternatives for energy storage will have to be investigated. To clearly identify the potential of any alternative for energy storage the results should not be diluted with application of energy saving devices. This would change multiple variables at the same time and could cloud the judgement of both their real contribution. Hence, energy saving devices like wind assisted sailing, improved anti-fouling and hydro-mechanic optimization will not be investigated in this project.

2.2 Boundary Conditions

2.2.1 Basic principle sustainable cycle

Renewable fuels are capable to comply with the principle of a sustainable cycle as presented in an example shown in Figure 2-1. Fuel options which are not capable to comply with the principle of the sustainable cycle are not included for comparison. Any energy requirement for production must come from renewable sources. In case of electrical energy, it should only be sourced from (the over capacity of) renewable energy. This way there are no harmful emissions related to the production.

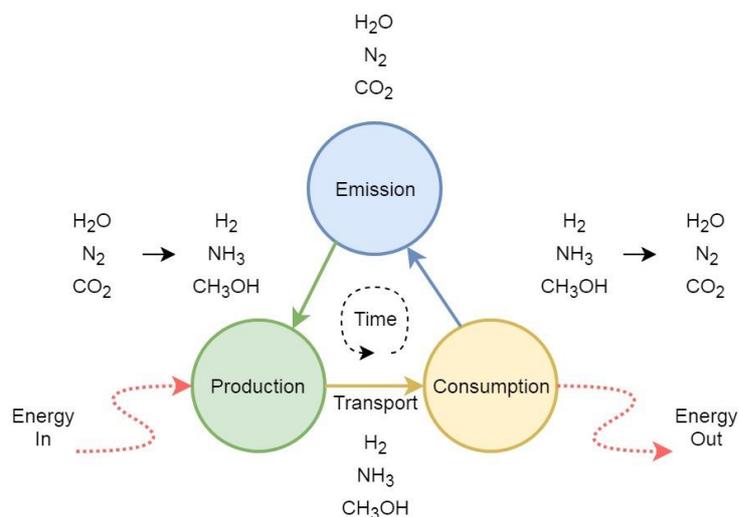


Figure 2-1: Sustainable cycle for renewable fuels (examples: Hydrogen, Ammonia and Methanol)

2.2.2 Biomass review

To review the potential of biomass one must first analyse if biomass is renewable and therefore compliant with the sustainable cycle. As indicated by an earlier study [1] (and in 2014 by the U.S. Environmental Protection Agency (EPA)) not all biomass is carbon neutral. For example, existing forests that may continue to grow if not used for bioenergy are not carbon neutral [1]. Cutting forests for

energy, either to burn trees or to plant energy crops, releases carbon into the atmosphere that would have been sequestered had the trees remained untouched, and the regrowing and thus recapture of carbon can take decades or even a century [2].

In some cases, biomass can be carbon neutral. For example, if fast growing crops are grown on otherwise unproductive land, in such a case the regrowth of the plants offsets the carbon produced by the combustion [2]. The requirement of otherwise unproductive land also covers the prevention of competition with the food industry which should always be avoided as this project hypothesizes on a truly sustainable future.

Due to the size of the maritime industry scalability is considered to be an important factor for renewable fuels. According to a large bioenergy assessment the most yield for carbon neutral biomass can be gained from dedicated crops [3]. This would mean significant amounts of otherwise unproductive land should be dedicated and utilized for growth of crops. Analysing the fuel demand for the maritime industry, the current consumption level is approximately 300 million tonnes per year [4] (distillate and residual types combined). By means of the lower heating value it can be converted to roughly 12.8 EJ per year. Based on the yield of 3 generally used bio mass types the required amount of otherwise unproductive land can be calculated as per Table 2-1.

Climate / Country (as example)	Type	Yield [W/m ²] [5]	Required otherwise unproductive land [km ²]	* United Kingdom [-]	* The Netherlands [-]
Temperate oceanic / United Kingdom	Rape seed	0.13	3,122,195	12.9x	75x
Temperate oceanic / United Kingdom	Sugar beet	0.40	1,014,713	4.2x	24x
Tropical / Brazil	Sugar cane	1.20	338,238	1.4x	8x

Table 2-1: Required otherwise unproductive land for biomass to supply the maritime industry

* The number of times the country could fit in the required otherwise unproductive land.

According to the bioenergy assessment [3] it is estimated that the sustainable technical potential of biomass can go up to 100 EJ by 2050, under high agreement. The Institute of Marine Engineering, Science and Technology (IMAREST) used this study in their report [6] submitted to the International Maritime Organization (IMO) for a meeting regarding reduction of greenhouse gases (GHG). In the report of IMAREST it is concluded that based on the biomass availability of 100 EJ, shipping would be able to use 4 to 11 EJ of this 100 EJ.

Although the 100 EJ as stated by the large bioenergy assessment is labelled 'high agreement' it is also noted that there are still significant uncertainties like technological development and ambiguity in political decision [3]. Furthermore, no specific justification on suitable land (not otherwise productive) is provided in the assessment. Reflecting on these facts and figures as shown earlier in Table 2-1 it is concluded that renewable bio mass alone is insufficiently scalable to supply the maritime industry. However, this does not mean fuels made from renewable biomass could not partially supply the industry. Yet due to the limited options in scalability only synthetic fuel production is included in the comparison of renewable fuels in the next section.

2.3 Renewable Fuel Options

2.3.1 Scalability

The scalability of renewable fuels can be expressed in an important economic factor for ship owners namely, fuel cost. Assuming a corresponding fully clean and sustainable future, synthetic fuels will be produced by means of the overcapacity of renewable energy. This means that fuel cost has a direct relation with the required energy to produce a fuel. Therefore, renewable synthetic production cost of a fuel is an important factor to compare renewable fuel options.

2.3.2 Storage properties

Besides fuel cost energy density and volumetric energy density are also important since cargo volume and deadweight are also important economic factors for ship owners. Furthermore, to keep the fuel storage as cost-effective as possible storage pressure and temperature are also relevant factors to use for comparison of renewable fuel options.

2.3.3 Comparison of renewable fuel options

Multiple renewable fuel options are compared considering, energy density, volumetric energy density, renewable synthetic production cost, storage pressure and storage temperature Table 2-2. (Consequences due additional volume and/or mass of the storage tank (shape) are not included.) When comparing ammonia to other renewable fuel options ammonia is considered as a balanced solution. Ammonia has a significant higher volumetric energy and has far more practical storage conditions, considering pressure and temperature compared to liquid hydrogen. Furthermore, ammonia requires clearly less energy for renewable synthetic production than the carbon carriers. These are the main reasons to further investigate the potential of ammonia as a marine fuel.

Fuel type	Energy density LHV [MJ/kg]	Volumetric energy density [GJ/m ³]	* Renewable synthetic production cost [MJ/MJ]	Storage pressure [bar]	Storage temperature [°C]
Marine Gas Oil (reference)	42.7 [7]	36.6	Not applicable	1	20
Liquid Methane	50.0 [8]	23.4	2.3	1	-162
Ethanol	26.7 [8]	21.1	3.6	1	20
Methanol	19.9 [8]	15.8	2.6	1	20
Liquid Ammonia	18.6 [9]	12.7	1.8	1 or 10	-34 or 20
Liquid Hydrogen	120.0 [8]	8.5	1.8	1	-253
Compressed Hydrogen	120.0 [8]	7.5	1.7	700	20

Table 2-2: Comparison of renewable fuel options

* The calculations and references of the used figures can be found in Appendix A.

2.3.4 Other

Other renewable fuel options are not included in the comparison either because they:

- Do not offer better overall properties in terms of (volumetric) energy and renewable synthetic production cost (for example HCO₂H/Formic acid).
- Are still too much in R&D stage (for example NaBH₄/Sodium borohydride or Si/Silicon).
- Are not known/are yet to be uncovered.

2.4 Conclusion

Ammonia is considered a balanced solution in terms of volumetric energy density and renewable synthetic production cost compared to other renewable fuels. Therefore, it will be investigated as marine fuel in this project. Currently conventional production of ammonia is based on natural gas. The onshore production of ammonia will have to switch over to renewable production to supply 'green' ammonia so it can be used as renewable fuel. This project will focus on the application of ammonia as a renewable fuel for the maritime industry. Production of renewable ammonia is out of scope of this project.

To realise the application of renewable ammonia a step wise implementation could be considered. This means rather than rapidly switching to 100% ammonia use as marine a fuel an ammonia diesel combination could be beneficial as an intermediate step. As diesel is a fossil fuel and thus not a renewable fuel it is out of scope of this research. The ammonia diesel combination will be reflected upon in the recommendations as comparison to the conclusions of 100% ammonia fuel.

3 ONSHORE TECHNICAL FEASIBILITY OF AMMONIA POWER GENERATION OPTIONS

This chapter will review the technical feasibility of multiple ways of onshore ammonia power generation. An overview of the options considered is given in Figure 3-1. In chapter 4 the general characteristics, of all the options which are technically feasible onshore, will be reviewed for marine applications. Chapter 4 will conclude with a selection of suitable options for marine applications. In chapter 5 the performance of the selection for marine applications will be studied and compared resulting in a final selection of one option to be compared with a conventional fuelled configuration in chapter 6. All safety related aspects will be covered in chapter 7 till 10.

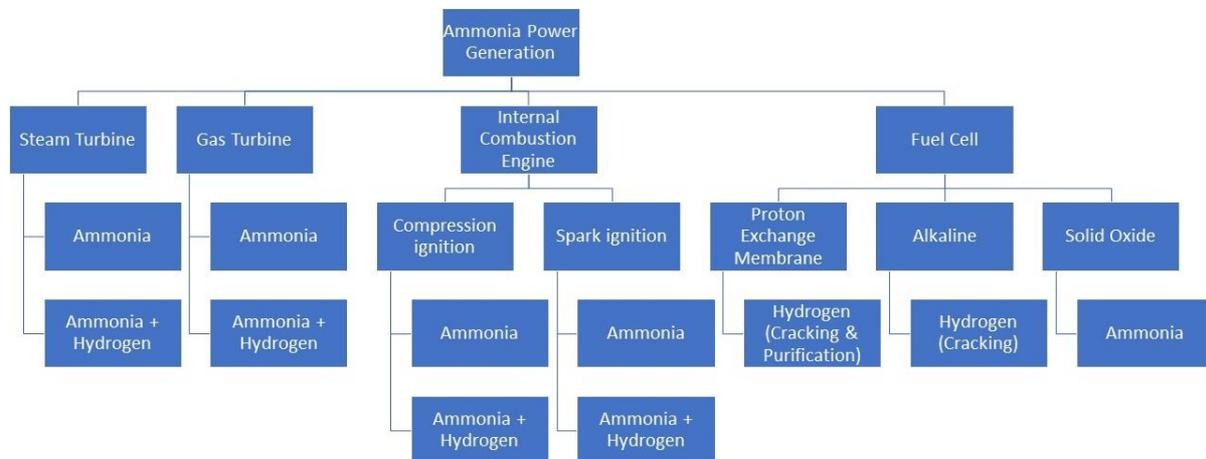


Figure 3-1: Ammonia power generation: Overview

3.1 Ammonia Combustion

Pure ammonia combustion has several challenges namely, high auto-ignition temperature (651°C), low flame speed, narrow flammability limits (15-28% by volume in air [10]) and high heat of vaporization [11]. To improve the overall combustion properties combustion of ammonia hydrogen mixtures are often also studied. Therefore, ammonia hydrogen mixtures are also included in this project. Ammonia hydrogen mixtures can be obtained by partially cracking the ammonia before injection.

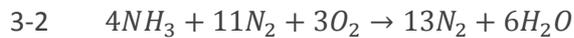
3.2 Steam Turbine

A steam turbine converts the thermal energy from pressurized steam into mechanical energy. The steam is made in a boiler by the heat released of combustion of a fuel creating a high-pressure area. After the turbine the steam goes through a condenser to create a low-pressure area which enables the steam flow to obtain sufficient speed. After the condenser the liquid water is reinjected into the boiler [12]. In order to study the feasibility of a fuel for a steam turbine the combustion of this fuel should generate sufficient heat to create steam.

3.2.1 Ammonia

By means of enthalpy of formation and Hess's law the lower heating value of ammonia can be calculated, resulting in 18.6 MJ/kg. See Appendix B for the calculation. With the combustion of ammonia heat is released. Since no heat is converted into work all the heat generated is available to generate steam by means of the heat in the exhaust gases. The basic reaction of ammonia combustion is shown in 3-1. Considering the fact that air is used rather than pure oxygen the mass distribution of the exhaust gases should be defined accordingly. In 3-2 air is approximated by a representative combination of nitrogen and oxygen. Combined oxygen and nitrogen cover 99% of the total air mass

which is considered to be a sufficiently accurate approximation of air. All the other gases in air are neglected.



The change in temperature, of the exhaust gases, can be calculated by the basic thermodynamic equation as shown in 3-3. See Appendix B for the calculation.

$$3-3 \quad Q = \sum_i (m_i \cdot c_{pi}) \cdot \Delta T$$

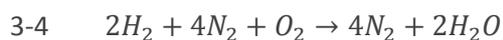
Where:

Q	Energy	J
m_i	Mass of component i	kg
c_{pi}	Specific heat of component i	J/kg·K
ΔT	Change in temperature	K

With the combustion of pure ammonia, the corresponding exhaust gases have a change in temperature of 1,637 K. This is considered to be more than enough to create super-heated steam assuming start condition of room temperature 293 K.

3.2.2 Ammonia + Hydrogen

Besides pure ammonia combustion in 3.2.1 an ammonia hydrogen mixture combustion is also examined. This is done by calculating the change in temperature of the exhaust gases of pure hydrogen combustion. The results of pure hydrogen combustion can be compared pure ammonia combustion to define a range of ammonia hydrogen mixture combustion. By means of enthalpy of formation and Hess's law the lower heating value of hydrogen can be calculated, resulting in 120.0 MJ/kg. The reaction of hydrogen combustion with air approximated by a representative combination of nitrogen and oxygen is shown in 3-4. See Appendix C for both calculations.



With the combustion of pure hydrogen, the corresponding exhaust gases have a change in temperature of 1,924 K. Considering ammonia hydrogen mixture combustion the exhaust gases would have an approximated range in change of temperature between 1,637 K and 1,924 K. Likewise with pure ammonia combustion, this is considered to be more than enough to create super-heated steam assuming start condition of room temperature 293 K.

3.2.3 Conclusion

Based on the basic thermodynamic calculations done in 3.2.1 and 3.2.2 it is clear that an ammonia fuelled steam turbine configuration is feasible.

3.3 Gas Turbine

A gas turbine uses a compressor that brings atmospheric air flows to a higher pressure. Energy is then added by spraying fuel into the air and igniting it so the combustion generates a high-temperature flow. This high-temperature high-pressure gas enters a turbine, where it expands down to the exhaust pressure, producing a shaft work output in the process [12].

3.3.1 Ammonia

Earlier research [13] indicated that pure ammonia combustion in a gas turbine with liquid injection had several limitations compared to hydrocarbon fuels. In the flame stability experiments, ammonia would burn at only half the air-flow velocity with hydrocarbon fuels and the range of equivalence ratios for stable flame was much narrower than for hydrocarbon fuels [13]. It was concluded that neat ammonia cannot be used as a substitute fuel for hydrocarbons in conventional gas turbine burners unless the ignition-system energy is increased, the combustion liner diameter is increased by a factor of approximately 2, and the ammonia injected in the gaseous state [13]. Furthermore, this research [13] also looked into combustion of partially dissociated ammonia which will be elaborated on in 3.3.2.

Other research [14] in the 1960's, Solar and UC Berkeley investigated a 250HP T350 (Technical Report DA-44-009-AMC-824(T)) single can ammonia burner turbine. Performance of the engine using ammonia vapour was found to be similar to JP-4. Using ammonia injection with equal power conditions compared to hydrocarbons the turbine inlet temperature was cooler than hydrocarbons [14]. This can also be confirmed with the basic thermodynamic calculations done for steam turbines. The mass of the exhaust gases of ammonia combustion at equal power conditions is higher than those of diesel. Furthermore, the percentage of water vapour in the exhaust gases of ammonia combustion is higher than those of diesel. Combined the higher total mass of exhaust gases and the higher percentage of water vapour, which has a significantly higher specific heat compared to nitrogen (and carbon dioxide for diesel), clarify the lower temperature at equal power conditions for ammonia combustion. In addition, when turbine inlet temperatures were matched to those of hydrocarbons, ammonia provided +10% increase power with high efficiencies [14].

In the research of Solar and UC Berkeley it was concluded that ammonia is satisfactory substitute for hydrocarbon fuels in a simple-cycle gas turbine engine. Rig test data developed for ammonia vapour combustor performance are satisfactory for use in design of engine combustors. Conversion of single combustor engines to ammonia fuel operation can be accomplished without major redesign and development effort. The complexity and cost of basic engines using ammonia vapour combustors will not be significantly greater than existing hydrocarbons burning engines. The addition of exhaust heat ammonia vaporizing systems to obtain system self-sufficiency will significantly increase size cost and weight [14].

3.3.2 Ammonia + Hydrogen

As discussed in 3.3.1 earlier research [13] of liquid ammonia injection in a gas turbine, applying partially dissociated ammonia was also studied. It concluded that ammonia with partially 28% dissociated ammonia could be used as substitute fuel in gas turbine combustion systems optimally sized for hydrocarbon fuels. The minimum ignition energy, quenching distance and flame-stability properties of 28% dissociated ammonia were approximately equal to these same properties of methane [13].

In more modern research work ammonia hydrogen blends has also been tested in a gas turbine burner [15]. To obtain similar laminar burning flame velocities as methane a 50% ammonia and 50% hydrogen mixture was used (for its specific condition of temperature, pressure and equivalence ratio). It was concluded that stable flames can be achieved with low emissions using strong swirling flows. Good correlation has been found with experiments and numerical calculations [15].

Other research has also indicated the benefits of using partially cracked ammonia, thus burning a mixture of ammonia and hydrogen. Using ammonia hydrogen blends improves the stability, efficiency, is capable of lowering NO_x emissions and has improved power loading conditions [16].

3.3.3 Conclusion

Reviewing the multiple studies done in the past and present the challenges of ammonia combustion have been acknowledged. Pure ammonia combustion in a gas turbine is feasible when applying ammonia vapour injection. Furthermore, the combustion properties can be improved by using ammonia hydrogen blends. Either way, applying ammonia or ammonia hydrogen blends in a gas turbine is feasible.

3.4 Internal Combustion Engine

An internal combustion engine combusts fuel with an oxidizer (usually air) in a combustion chamber. In an internal combustion engine, the expansion of the high-temperature and high-pressure gases produced by combustion applies direct force to pistons of the engine. This force moves the piston over a distance, transforming chemical energy into useful mechanical energy [12].

3.4.1 Compression ignition (Ammonia)

In 1967 a Cooperative Fuel Research (CFR) engine using a compression ignition scheme with liquid ammonia injected directly into the cylinder has been operated [17]. In order to achieve successful autoignition of ammonia, the compression ratio of the engine needed to achieve 35:1 with jacket and intake air temperatures at 150°C [17].

More recently a simulation study has been conducted to explore if the intake air temperature and compression ratio could be lowered by means of two stage injection: a pilot injection and a main injection [18]. Using compression ratio conditions up to 30:1 resulted in less than 90% combustion efficiency for all start main injection timing conditions [18]. This study did show NO emissions can be reduced by 25% under certain conditions. Yet this reduction did result in a considerable amount of ammonia slip. Therefore, it was concluded that the start of pilot fuel injection should be adjusted with precisely to avoid large amounts of ammonia slip and reduce NO emissions accordingly [18].

3.4.2 Compression ignition (Ammonia + Hydrogen)

Recent published research showed that stable combustion in a Homogeneous Charge Compression Ignition (HCCI) can be achieved up to 70%vol ammonia and 30%vol hydrogen with a compression ratio of 16:1 [19]. With the use of ammonia hydrogen mixtures, it was noted that a trade-off between high compression ratio to promote ammonia combustion and a limited compression ratio to prevent hydrogen from ringing is needed [19]. Ringing occurs in HCCI engines when the combustion intensity is too high: an local auto-ignition inducing a gas expansion at the speed of sound that oscillates inside the cylinder [20] [21]. Even though it occurs through a slightly different mechanism than spark ignition knock, the consequences are similar [19]. An electric motor was coupled to the engine to set the rotational speed, in this study fixed at 1,500 rpm [19].

3.4.3 Spark ignition (Ammonia)

Combustion of ammonia in SI-engine can be facilitated by having stronger igniters, compacted combustion chamber and longer spark plugs in order to overcome ammonia's reluctance to combustion [22].

Ammonia only as fuel has also been patented by Toyota where they suggest that several plasma jet igniters arranged inside the combustion chamber or plural spark plugs that ignite the ammonia at several points will facilitate ammonia combustion [23].

In 2011 computerized models were studied where ignition of ammonia was achieved by an electric arc of about 2 kV in one of the tests [24]. Ammonia as the only fuel in a spark ignition engine has not been

realized at a serious level. Suggestions have been made without any further steps to make this technology feasible in existing vehicles [11]. Besides computerized studied model an experimental study has also been conducted using a four-stroke single cylinder VARIMEX test engine of 814 cc [24]. The compression ratio of this test engine can be varied from 8:1 to 19:1. Test results have been presented for compression ratios of 13:1, 15:1 and 17:1. It was concluded that the optimum running conditions were obtained at a compression ratio of 15:1. These conditions were considered to be the best trade-off to reduce unburned ammonia, about 8%, reduce NO emissions approximately 800ppm and reduce hydrogen slip about 4000 ppm due to dissociation of ammonia [24].

3.4.4 Spark ignition (Ammonia + Hydrogen)

In 2016 a research was conducted using a spark ignition engine with an ammonia hydrogen mixture [10]. The engine was a twin cylinder 505 cc with a compression ratio of 10.7:1 and is operated between 2,500-5,000 rpm with an output of 14 kW @ 5,000 rpm (using ammonia hydrogen mixture). Appropriate direct injection strategies were developed to allow ammonia to be used in spark-ignition engines without sacrifice of volumetric efficiency. The use of ammonia hydrogen mixtures as an SI engine fuel was investigated in the same context [10].

The octane rating of both ammonia and hydrogen is higher than gasoline, making it preferable to run at a higher compression ratio (CR). The flame velocity and the minimum ignition energy of ammonia and hydrogen are far apart. By mixing it was hoped that a suitable compromise could be gained. The ammonia to hydrogen ratio presents a new possible engine control parameter [10]. Ammonia represents a hydrogen carrier and can be effectively utilized as fuel in IC engines, provided that a small percentage of other fuels is added as combustion promoter. Among them, the best one is hydrogen, which can be obtained directly from ammonia on board the vehicle by means of a catalytic reformer [10].

The experimental results confirm the need to speed combustion up by adding hydrogen to air-ammonia mixture, with ratios that mainly depend on load and less on engine speed. Exhaust pollutant emission (only NO_x) is low, with a maximum of 1,700 ppm at full load and 3,000 rpm [10].

Besides this research a more recent usage of ammonia hydrogen mixtures in a SI engine has been shown by Siemens. Siemens has a 'Green Ammonia energy storage system demonstrator' test facility where their engine (with a compression ratio of 11.6:1) is used in combination with a generator to provide electrical energy from ammonia [25] [26].

3.4.5 Conclusion

Reflecting on the studies done on ammonia fuelled combustion engines it is clear all options are feasible. Yet pure ammonia combustion has its limitations in performance compared to ammonia hydrogen fuelled mixtures.

3.5 Fuel Cell

A fuel cell is an electrochemical cell that converts the chemical energy from a fuel into electricity through an electrochemical reaction of fuel with oxygen or another oxidizing agent. Fuel cells are different from batteries in requiring a continuous source of fuel and oxygen (usually from air) to sustain the chemical reaction [27].

Proton Exchange Membrane Fuel Cells (PEMFC) and Solid Oxide Fuel Cells (SOFC) have been identified as most promising by both general market studies [28] [29] and a fuel cell marine application study done by DNV-GL [30]. Therefore, PEMFC and SOFC are reviewed in this project. In addition, Alkaline

Fuel Cells (AFC) are also considered as they are an intermediate solution between the PEMFC and SOFC when applying ammonia as fuel.

3.5.1 Proton Exchange Membrane (Hydrogen (Cracking & Purification))

PEMFC's are commercially available from multiple manufacturers and have been applied in multiple types of transport like cars, buses and light trains and submarines [31] [32] [33]. A PEMFC can only use pure hydrogen as fuel so when applying ammonia as source cracking and purification of ammonia is required. CSIRO has realised a pilot plant where ammonia is first decomposed in a cracker and then purified in a membrane resulting in PEMFC grade hydrogen [34]. Other companies are also active commercializing similar technology [35] [36].

3.5.2 Alkaline (Hydrogen (Cracking))

Like the PEMFC an AFC can also only use hydrogen. Yet, an AFC does not require the strict purity which is needed for a PEMFC. This means only cracking without purification of ammonia is sufficient to supply an AFC. GenCell has developed an AFC with a cracker which is capable of using ammonia as a fuel [37]. GenCell also commercialized this system and announced its first commercial customer in July 2018 [38]. ZBT (Zentrum für BrennstoffzellenTechnik) also successfully developed and tested an ammonia fuelled system using a none electrical cracker and an AFC with their project ALKAMMONIA [38] [39].

3.5.3 Solid Oxide (Ammonia)

Different from the PEMFC and AFC the SOFC is capable of using ammonia directly preventing the need for cracking and purification. SOFCs able to use ammonia are available but currently only used for lab experiments. Research done by Università degli Studi di Perugia has indicated that successful operation with high efficiencies and no NO_x formation can be achieved [40]. In 2017 the Kyoto University announced it attained 1000 hours of continuous operation of an SOFC fuelled by ammonia [41].

3.5.4 Conclusion

With successful operation of the PEMFC, AFC and SOFC either in experiments or commercial applications it is concluded that all 3 types are feasible.

3.6 Conclusion

It is concluded that all onshore ammonia power generation options considered are technically feasible, as shown by Figure 3-2. In chapter 4 each option will be reviewed if it is suitable for marine applications based on general characteristics including fuel type and scalability.

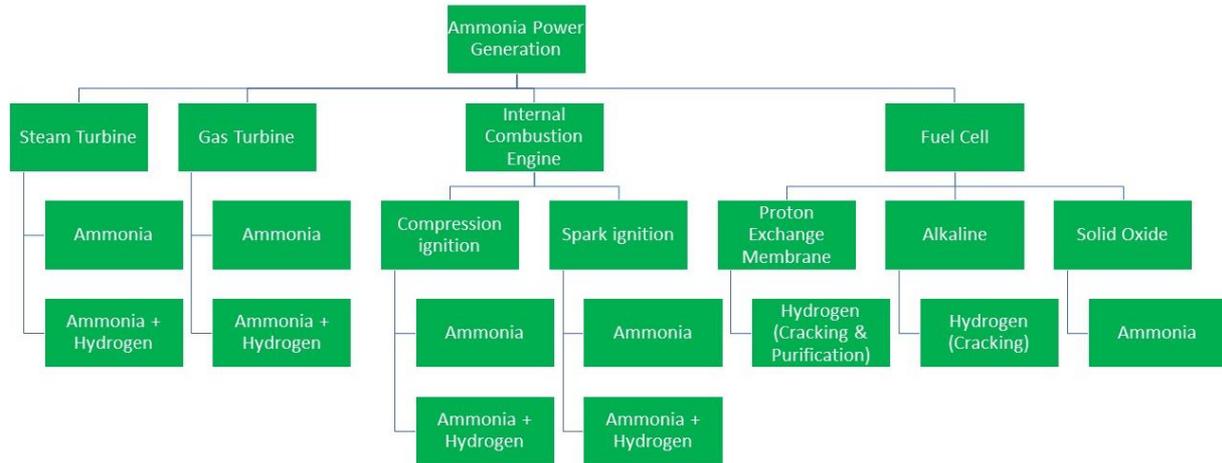


Figure 3-2: Ammonia power generation: Selection of onshore technically feasible options

4 MARINE TECHNICAL FEASIBILITY OF AMMONIA POWER GENERATION OPTIONS

In this chapter each ammonia power generation option will be reviewed to determine if it is suitable for marine applications based on general characteristics including fuel type and scalability.

4.1 Ship Type

This project is looking into ammonia as a fuel for the maritime industry. For ship owners' cost and availability of alternative fuels is a serious struggle for adoptions of alternative fuels. Therefore, it is considered that ships that carry ammonia in bulk are most suitable as first vessels to use ammonia as fuel. Similar steps have been made with Liquid natural Gas (LNG) tankers. With conventional marine fuels becoming more expensive than natural gas in combination with more strict emission regulations, more and more LNG tankers use their cargo as fuel.

With ammonia carriers selected as vessel type for this project the concept design can be defined. Ammonia carriers are currently mainly known as Liquid Petrol Gas (LPG) tankers. The LPG tankers are capable of transporting more than one kind of cargo since the storage conditions of both LPG and ammonia, like temperature and pressure, are very similar.

Ammonia can be transported in liquid form either fully pressurized, 10 bar at 20°C, fully refrigerated -34°C at 1 bar or semi pressurized/refrigerated were the pressure needs to be higher than the vapour pressure. To cover the influence of each of these storage conditions 3 ammonia carriers have been determined, each with its own capacity. Based on reference vessels, see Appendix D, the concept ammonia carriers have been defined as shown in Table 4-1 and Table 4-2. These ammonia carriers will serve as a basis to compare the performance of each option. Studying the reference vessels and defining the concept ammonia carriers has been done by research efforts prior to the start of the thesis.

Storage type	DWT [ton]
Fully pressurized	6,000
Semi pressurized/refrigerated	18,000
Fully refrigerated	54,000

Table 4-1: Ammonia carrier type & selected size

DWT [ton]	6,000	18,000	54,000
Loa [m]	120.0	166.0	239.0
Lwl [m]	115.0	157.0	229.0
Bmld [m]	18.0	25.8	35.0
T [m]	6.0	8.4	11.8
D [m]	10.0	18.7	21.8
Displacement [ton]	9,600	26,100	72,900
Design speed [kts]	14	15	16
Propeller shaft (full) [kW]	4,500	6,500	11,500
Bow thruster [kWe]	300	400	600
Hotel power [kWe]	130	180	260
Re-liquefaction power [kWe]	0	350	1,050

Table 4-2: Ammonia carrier main particulars

The ammonia carrier concept designs are based on the average main particulars of the reference vessels and are therefore considered to be a market representative. The main interest is to identify the difference in performance of ammonia fuelled vessels compared to conventional fuel. Therefore, there will be no specific further optimization.

With the ship type selected, an ammonia carrier, there is a clear preference of efficiency over power density. Reviewing reference vessels saving fuel cost is more dominant than the required space and mass for the power generation system.

4.2 Steam Turbine

The steam turbine has been used in the past for marine propulsion but has lost ground because it has low power density and is less efficient compared to the gas turbine and internal combustion engine [12]. Therefore, the steam turbine will not be further investigated in this project.

4.3 Gas Turbine

In the beginning of 1970, the gas turbine superseded the steam installation as propulsion for naval ships as it has a higher power density and higher efficiency [12]. Modern naval vessels still use gas turbines to sail at high speed [42] as it is favoured mainly for its higher power density. However, the internal combustion engine is most commonly used for power generation onboard vessels due to the fact gas turbines are less efficient. Therefore, the gas turbine will not be further investigated in this project.

4.4 Internal Combustion Engine

4.4.1 Fuel

Applying ammonia or ammonia hydrogen mixtures is feasible in internal combustion engines as presented in 3.4. Like with the gas turbine, similar difficulties have been encountered with pure ammonia combustion in internal combustion engines. Although pure ammonia combustion is feasible there are several aspects which makes pure ammonia less favourable than ammonia hydrogen mixtures. Performance aspects like high compression ratio for CI and low flame speed, low flame stability, limits in operation to cope with ammonia slip (lower combustion efficiency) and NO_x emissions for both CI and SI make pure ammonia less suitable than ammonia hydrogen mixtures for marine applications. Therefore, only ammonia hydrogen mixtures in internal combustion engines will be investigated further in this project.

Ammonia hydrogen mixtures can be used in a (HC)CI and SI internal combustion engine. Based on their principle design the HCCI is bound to certain mixtures and their corresponding timing. Furthermore, to use both fuels efficiently the HCCI has a trade-off between a high compression ratio to promote ammonia combustion and a limited compression ratio to prevent hydrogen from ringing. Considering these aspects, the SI internal combustion engine offers more flexibility in design and operation. If this additional flexibility is required for proper operation in marine applications is something for an engine manufacturer to investigate further. For this project ammonia hydrogen mixtures in internal combustion engines will be further investigated for marine applications. No ignition type will be specified as preferable. However, to proof scalability reference to a particular type can be used but does not mean it excludes the other.

4.4.2 Scalability

As discussed with gas turbines in 3.3 ammonia hydrogen mixtures can obtain similar combustion properties as methane. These properties are also of value when considering applying ammonia

hydrogen mixtures in internal combustion engines. Natural gas, which is more than 90% (mol) methane, can be considered relatively new as marine fuel compared to the conventional crude oil based Marine Gas Oil (MGO) and Heavy Fuel Oil (HFO). However, in the past decade several dual fuel [43] and pure gas [44] engines have been developed and successfully operated on numerous small and large vessels.

Based on the experience of marine applications with natural gas fuelled internal combustion engines and the capability of ammonia hydrogen mixtures to obtain similar combustion properties as methane, it is concluded that internal combustion engines fuelled by ammonia hydrogen mixtures are technically feasible for marine applications. In addition, MAN Energy Solutions recently presented at the Ammonia Energy Association conference. MAN sees potential in ammonia as a marine fuel and claimed that within 2 years a two-stroke marine scale ammonia powered engine could be development [45]. However, this will only be done if MAN has a customer for such an engine. Nevertheless, the fact that MAN considers an ammonia powered marine scale internal combustion engine technically feasible is a welcome addition to the conclusion of this project. (Besides conventional marine fuels MAN has experience with several alternative fuels like Liquid Natural Gas (LNG), Liquid Petroleum Gas (LPG) and methanol.) Specific marine performance of internal combustion engines using ammonia hydrogen mixtures will be studied and compared with other types of ammonia power generation in chapter 5.

4.5 Fuel Cell

4.5.1 Fuel

Both PEMFCs and AFCs are only capable to use hydrogen as fuel, so no comparison and selection of fuel is required or possible. The SOFC is capable to use multiple fuels, considering the scope of this project this covers ammonia and hydrogen (obtained from cracking ammonia). Cracking ammonia to obtain hydrogen before fuelling the SOFC would not make sense since fuelling the SOFC with ammonia directly, allowing the ammonia to be cracked inside the SOFC, is more efficient. So, for each fuel cell type the fuel type is fixed in this project (as indicated in chapter 3).

4.5.2 Scalability

A single fuel cell stack of all types considered on megawatt scale is not available. So, for fuel cells to be applied on vessels multiple stacks will have to be installed to meet the power demand of a vessel. Fuel cell stacks are modular so stacking multiple across the vessel is possible. The considered fuel cells are capable of power generation without producing any harmful emissions using ammonia as primary fuel source. Furthermore, the efficiency for electric power generation is high. Nowadays, one or more of the considered fuel cell types have a low power density and cost significantly more than an internal combustion. However, future development could improve this thus maintaining the interest of the overall performance. Therefore, all three types will be studied in chapter 5.

4.6 Conclusion

Of all the options considered at the start of chapter 3 the green marked options in Figure 4-1 are qualified as (sufficiently) technically feasible for marine application. In chapter 5 the marine performance of these options will be studied.

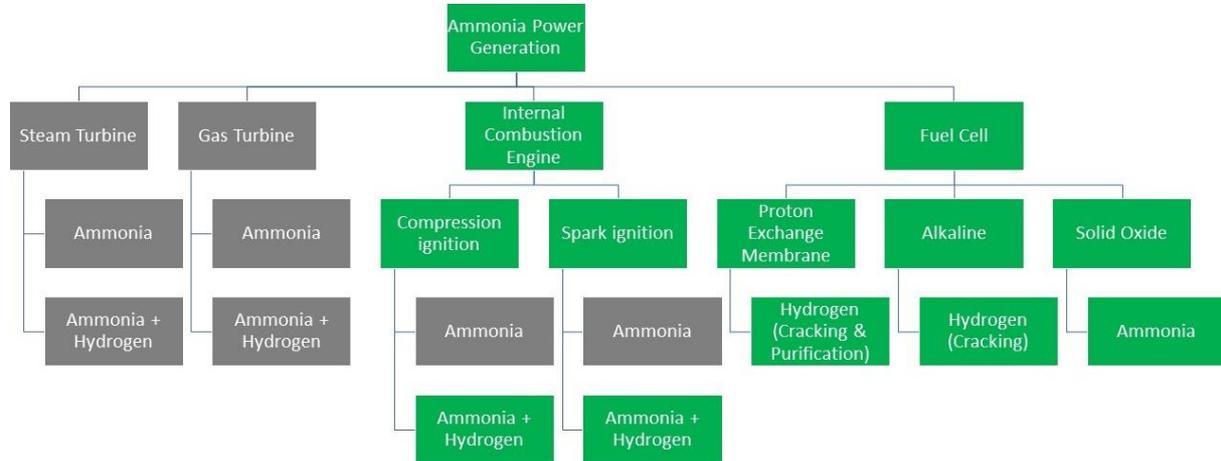


Figure 4-1: Ammonia power generation: Selection of marine technically feasible options

5 MARINE PERFORMANCE OF AMMONIA POWER GENERATION OPTIONS

In this chapter the marine performance of the selection made in chapter 4 will be studied and compared. At the end of this chapter a final selection of the best option will be made to be compared with a conventional fuelled configuration in chapter 6.

5.1 Performance Indicators

To study the marine performance of each option only the largest ammonia carrier, 54,000 ton DWT, will be used. The other two will be added in chapter 6 to compare the best ammonia powered option with the conventional configuration to also study the influence of boil off on cost-effectiveness. With the ship type selected the relevant performance indicators can be addressed. In this section each performance indicator will be explained. Safety is not included in the performance indicators in this chapter. Nevertheless, safety is considered to be a very important performance indicator. Therefore, it is addressed separately in chapter 7 till 10 as mentioned in the introduction of chapter 3

5.1.1 System definition

To clearly assess each option all crucial primary aspects of the systems are provided in this subsection. Covering system design in a flow chart and a table with load definition of the design condition including its distribution.

5.1.2 Power density

A vessel is a mobile application and like other mobile applications available space and mass for equipment is limited. Therefore, density of systems, in this case the power generation system, on board is relevant. This project will focus on the main component of the power generation system considering power density covering both mass [kW/kg] and volume [kW/m³]. Additional impact on power density due to different support systems is out of the scope of this project. This is something to be further investigated in a later design stage.

5.1.3 Harmful emissions

With the goal of applying ammonia to significantly reduce and eventually eliminate harmful emissions the topic of emissions is very important. The main harmful emissions due to power generation on board vessels are carbon dioxide (CO₂), nitrogen oxides (NO_x), sulphur oxides (SO_x) and particle matter (PM) [46]. Furthermore, fuel slip is also considered to be of importance. Other emissions such as sewage, ozone-depleting substances (ODSs) other than NO_x, volatile organic compounds (VOCs) and emissions due to shipboard incineration are not considered relevant for this project since only power generation by means of an alternative fuel is studied.

Considering the possibility of fuel slip both ammonia and hydrogen could be emitted into the atmosphere. Ammonia itself is not a greenhouse gas but it is a toxic gas. Therefore, ammonia slip as an emission is important and will be one of the indicators regarding harmful emissions. Hydrogen is an indirect greenhouse gas [47]. The expected improvement in global warming gained from replacing fossil fuel-based economy with a hydrogen-based economy would not be fully realised unless hydrogen leakage is carefully controlled [47]. In respect of impact it was concluded that a leakage rate of 1% hydrogen has a climate impact of 0.6% of the fossil fuel system it replaces [47]. For this project however, the significance of hydrogen slip is considered insufficient and will not be studied for this project. It is recommended to check hydrogen slip in a later design stage.

With the combustion of ammonia NO_x emissions can occur. Therefore, NO_x emissions will be one of the indicators regarding harmful emissions. Ammonia is carbon and sulphur free. Using ammonia as a

fuel does not produce CO₂, SO_x or PM emissions [24]. Therefore, the emissions levels of CO₂, SO_x and PM, are zero and will not be further investigated per option.

5.1.4 Load response

The selected ship type, an ammonia carrier, is a bulk carrier transporting ammonia as cargo. The required load response for a bulk carrier is moderate. A tug has a significant load response requirement as it has high peak loads over short periods of time. A cargo vessel, which is mainly in continuous transit condition, has moderate load response requirements as the load fluctuations, for example during heavy weather with loads fluctuating on the propeller, are less severe compared to the operational profile of a tug. Besides load fluctuations due to heavy weather the capability for a decent ramp up and down to operate around ports is also of importance for a bulk carrier. Therefore, load response is a performance indicator.

5.1.5 Part load conditions

In and around ports a bulk carrier needs to be able to operate on part load conditions. Therefore, the minimum rotational speed and torque or minimum power output is a performance indicator.

5.1.6 Marine environment

Ships are exposed to the marine environment. For power generation systems relevant marine environment conditions are accelerations and salty air. Therefore, the capability to cope with these conditions is a performance indicator.

5.1.7 System efficiency

The efficiency of the power generation system has a significant influence on the vessel design and its operational cost. Therefore, the efficiency is an important performance indicator.

5.1.8 Total cost of ownership

The total cost of ownership is an important factor for ship owners to select a power generation system. Therefore, total cost of ownership is a performance indicator.

As this project focusses on the difference in performance only the part that is different from the conventional basis will be calculated in Capital Expenditures (Δ CAPEX) and Operational Expenditures (Δ OPEX). Therefore, the total cost of ownership (Δ TCO) will also only indicate a price difference between each option and does not cover all the cost for the entire ship.

The Δ TCO consists of both Δ CAPEX and Δ OPEX. The Δ CAPEX consists of the purchase cost of the power generation system. The Δ OPEX is based on 25 years of operation in the design condition with 6500 running hours per year. The Δ OPEX consists of the maintenance cost of the power generation system, fuel cost and less income since a part of the cargo is used for fuel.

The fuel cost is based on the cost of green ammonia which could be realised in the short term, 850 euro/ton [9]. In the future green ammonia can be produced for approximately 400 euro/ton [9] as the electricity price is expected to be within a range of 2-3 eurocent/kWh when utilizing the overcapacity of renewable energy. The 850 euro/ton will be used in this chapter to compare each option. The comparison of the selected option with the conventional configuration will cover both 850 euro/ton and 400 euro/ton.

Less income is taken into account by means of a factor covering less income per ton less cargo transported. This factor is calculated by dividing the total OPEX of the conventional option by the effective DWT for cargo. This factor is then multiplied with the less cargo transported in each option defining the lost income yearly.

5.2 Internal Combustion Engine

5.2.1 System definition

5.2.1.1 Engine type

The most common internal combustion engine type used in bulk carriers is a slow speed two-stroke engine. The main advantage is that a slow speed engine, with rotational speeds between approximately 60-190 rpm, can be directly connected to the propeller shaft without a gearbox. Without a gearbox the overall efficiency is generally up to 2% higher reducing fuel cost. Furthermore, large slow speed engines generally have a higher engine efficiency. Slow speed two-stroke engines do have a lower power density compared to the medium/high speed four stroke engines which do use a gearbox. For this project efficiency is considered more important than power density as discussed 4.1. Therefore, a slow speed two-stroke engine is selected for the option of the internal combustion engine. The four-stroke type will not be investigated as main engine for this project.

5.2.1.2 Propeller

The options for the propeller are either a Fixed Pitch Propeller (FPP) or a Controllable Pitch Propeller (CPP). Theoretically the FPP has a higher efficiency than a CPP. However, the CPP offers more manoeuvrability as it is capable of delivering zero thrust while it is rotating and connected to the engine where the FPP configuration has a minimum thrust. For this project efficiency is considered more important than the manoeuvrability that can be gained from a CPP. Therefore, an FPP is selected.

5.2.1.3 Electrical system

During normal continuous operation the main engine also generates electrical power by delivering power to the shaft generator via the Power Take Off (PTO). As the propeller is an FPP there is no single rotational speed that is constantly provided to the PTO. Therefore, for this project it is considered required to apply a frequency converter so the flexibility in using the shaft generator is not limited by the rotational speed of the engine. The provided electrical power is distributed by a switchboard and where needed, depending on the particular system, a transformer is applied to adjust the voltage. To simplify the system, it is assumed that all systems use the transformer as a conservative approach.

5.2.1.4 Overview

This project focusses on the transit/design speed condition to compare options with each other. Operation in and around ports or any other condition a generator might be required is out of the scope of this project. An overview of the design condition and distribution is given in Table 5-1.

Load type	Main engine		***Generators [kWe]
	Propeller shaft [kW]	PTO – *Delivered [kW] – [kWe]	
Propeller shaft	11,500		
Main engine support		486 – 430	
Hotel		**294 – 260	**260
Bow thruster			****600
Re-liquefaction			****1,050

Table 5-1: Design condition and distribution, ICE option

5.2.2 Power density

The rate of heat release and the stability of the flame to propagate are both relevant for power density. In addition, the total air (and fuel) demand to release a certain amount of energy also has an influence on the power density. As discussed in 3.3 ammonia hydrogen mixtures can obtain similar properties as methane in both flame stability and flame speed. As mentioned in 4.4 natural gas is more than 90% (mol) methane. Therefore, the stoichiometric combustion of both ammonia, hydrogen and methane are compared as shown in Table 5-2.

Fuel type	Ammonia		Hydrogen		Methane
Output [MJ]	18.6	50.0	120.0	50.0	50.0
Fuel input [kg]	1.0	2.7	1.0	0.4	1.0
Air input [kg]	6.1	16.4	34.3	14.3	17.2
Total input [kg]	7.1	19.0	35.3	14.7	18.2

Table 5-2: Stoichiometric combustion comparing: Ammonia, Hydrogen and Methane (white columns chemical properties, blue columns comparison of equal energy content)

The comparison shows that ammonia hydrogen mixtures are within a similar range of air mass input (and total mass input) as methane. Therefore, it is assumed for now that an ammonia hydrogen engine has a similar power density as a natural gas engine. Further investigation, which is out of scope of this project, should be done by for example an engine manufacturer to check this assumption. Multiple aspects like, but not limited to, sensitivity to knocking and its relation to required air excess ratio could influence the power density.

Based on the engine for the 54,000 ton DWT ammonia carrier the resulting power density is 38 kW/ton and 29 kW/m³. These figures are based on simplified measurements and are only used as guideline for comparison [51]. See Appendix E for the calculation.

5.2.3 Harmful emissions

5.2.3.1 NO_x

Based on the literature as discussed in 3.4 the resulting NO_x emissions of small-scale engines using ammonia hydrogen mixtures can be found in Table 5-3.

Engine	PSA DW10 (HCCI) [19]	Lombardini LGW 523 MPI (SI) [10]	CFR (SI) [52]
Power output [kW]	-	14	-
Cylinder volume [cm ³]	499	505	613
Rotational speed [rpm]	1500	2500-5000	1200
Compression ratio [-]	16:1	11:1	6:1 – 14:1
Air excess ratio [-]	-	-	0.9 – 1.6
Ammonia / Fuel volume [%]	0 – 61	-	0 – 95
NO _x [ppm]	750 – 2000	1500 – 1700	500 – 5500
*NO _x [g/kWh]	1.9 – 5.0	3.0 – 3.4	0.5 – 7.7

Table 5-3: Small scale ammonia lab test engines

*Approximated based on conservative assumption of air excess ratio: 2.5 (if not provided).

In comparison, diesel engines generally perform between 8 and 14 g/kWh. The power scale (100 kW vs 20 MW) of the diesel engine has little influence on NO_x emissions in terms of g/kWh. This can be

seen when one compares NO_x emissions of diesel fuelled cars and marine diesel engines with similar rotational speed. Both small scale diesel engines in cars and marine diesel engines with a rotational speed above 2000 rpm are around 8 g/kWh NO_x emission [46] [53] [54], also see Appendix F. Slow speed marine diesel engines have higher NO_x emissions in term of g/kWh, generally around 14 g/kWh [46] [48], even though they are more efficient. This is due to the fact NO emissions, which are generally the dominant form of NO_x emissions, are mainly kinetically controlled which means the residence time has a big influence [55].

In order to estimate the NO_x emissions of large marine scale engines using ammonia hydrogen mixtures the principle differences in respect to NO_x emissions of ammonia hydrogen mixtures compared to diesel need to be defined. Nitrogen oxides are mainly reaction products from the nitrogen and the oxygen in the air formed under high temperatures [55]. In addition, for diesel engines, a substantial part of fuel bound nitrogen is converted to NO_x as well [55]. Since ammonia contains significantly more nitrogen than diesel the NO_x emissions could definitely be higher.

Local high temperatures in the post flame zone are responsible for NO formation [55]. In order to avoid high NO_x emissions, the peak temperatures should be lowered [55]. However, in diffusion flames this leads to a higher particulate matter and hydrocarbon emissions, when using diesel [55]. This trade-off is often referred to as the “diesel dilemma” [56]. Using ammonia hydrogen mixtures does not have this issue and therefore can reduce NO_x emissions by freely lowering peak temperatures. Furthermore, as was discussed earlier in 3.2 and 3.3 the exhaust gas temperature of ammonia hydrogen mixtures is lower compared to hydrocarbons. The fact that the overall exhaust gas temperature is lower, and the design can be freely adjusted to reduce peak temperatures, are both valuable aspects to lower NO_x emissions for ammonia hydrogen mixtures.

Since NO_x is formed primarily in the high temperature zones a better distribution (more homogenous) of the air fuel mixture is desirable [55]. Diesel is not premixed during the compression stroke but injected later. The ammonia and hydrogen are premixed with air making it more desirable regarding lower NO_x emissions compared to diesel.

In relation to the other emission fuel slip, in this case ammonia, can also influence the NO_x emissions. In the literature study as discussed in 3.4 a decrease in NO_x emissions was found with an increase in ammonia proportion [19]. No factual proof could be brought for this observation, although the authors of [19] believe it is linked to an increased ammonia concentration in the exhaust gases. Indeed, as the ammonia proportion at the intake increases, the unburned ammonia concentration increases. Consequently, either the measurement method (chemiluminescence) was flawed because of the ammonia content in the sampled gases, or some Selective Non-Catalytic Reduction (SNCR) took place during the expansion stroke [19]. Indeed, chemiluminescence for NO_x measurement has already been shown to be affected by ammonia presence [57] and SNCR is known to happen in presence of ammonia and NO_x at temperatures around 700 K [58], as during the expansion stroke. It is to be noted that both phenomena can have occurred [19].

Reviewing the data given in Table 5-3 and the presented NO_x emissions of diesel engines it can be observed that ammonia hydrogen mixtures and diesel perform similar on high-speed small-scale engines. So, even though there is more nitrogen in present in the fuel the other factors of lower exhaust gas temperature, more freedom to reduce peak temperatures, more homogenous charge of fuel and air, and the possible influence of SNCR due to ammonia slip seem to even out their influence on NO_x emissions, resulting in similar performance as diesel engines.

In conclusion, several engine parameters can influence the NO_x emissions. Currently insufficiently is known to determine an accurate number on the NO_x emissions levels of large marine engines. It is recommended that further study should be done, by for example an engine manufacturer to obtain more knowledge on this topic. Specific engine design is out of the scope of this project. Therefore, based on the given data, it is assumed that the defined system, a slow speed two-stroke marine engine fuelled with an ammonia hydrogen mixture, has similar performance in NO_x emissions as diesel, approximately 14 g/kWh.

5.2.3.2 Fuel slip

To principally reduce fuel slip it is important to have the correct air excess ratio. The air excess ratio should be sufficiently above 1 so all fuel has enough oxygen to realise combustion. On the other hand, the air excess ratio should not be too high as too much air can lead to misfiring. In addition, exhaust valve and fuel injection timing should be carefully monitored to prevent fuel leaving the cylinder before compression. Both these aspects should be further investigated by for example an engine manufacturer as they are out of the scope of this project. This project intends to establish an assumption based on available literature as guideline.

Research mentioned in 3.4 covered pure ammonia combustion in an SI engine. Results indicated that there was approximately 2% ammonia (percentage of exhaust gas composition) slip occurred (which is approximately 8% unburned ammonia) [24]. Reflecting on research with ammonia hydrogen mixtures the combustion efficiency is significantly higher than pure ammonia [10]. Operation of the test engine with ammonia hydrogen mixtures had less than 100 ppm of ammonia slip [10]. As mentioned in 5.2.3.1 NO_x emissions combined with ammonia slip could mitigate each other by means of SNCR.

The cracker produces nitrogen, hydrogen and uncracked ammonia from the ammonia supply. The hydrogen and ammonia are used in the internal combustion engine. The nitrogen is separated upfront accordingly and redirected to the exhaust. For this project it is assumed that separating the nitrogen from the hydrogen and ammonia can be done without any fuel slip. This is something to be further investigated in a later design stage.

Currently insufficiently is known to determine an accurate number on the ammonia slip levels for a slow speed two-stroke engine using an ammonia hydrogen mixture. For now, it is assumed the ammonia slip levels of a slow speed two-stroke engine are below 100 ppm. A possible aid could be additional air supply in the exhaust system to promote complete combustion. As mentioned in the first paragraph of this sub-subsection fuel slip should be further studied.

5.2.4 Load response

5.2.4.1 Engine

The rate of heat release and the capability to cope with fluctuating air fuel and air excess ratios are both important for load response. Likewise, with power density as discussed in 5.2.2 the fact that ammonia hydrogen mixtures can obtain similar properties as methane in both flame stability and flame speed is also important for load response. Therefore, for now it is assumed that an ammonia hydrogen engine has a similar load response as a natural gas engine. Further investigation should be done by the engine manufacturer to check this assumption.

Earlier research has indicated that lean-burn pre-mixed combustion typically results in higher cycle-to-cycle fluctuation of cylinder pressures compared to diesel combustion [59]. During the natural gas

(dual fuel) engine demonstrator test, with a slow speed two-stroke engine of 19 MW, it was found that the cycle-to-cycle fluctuation of maximum cylinder pressures is higher than in diesel mode. However, indicated mean effective pressure fluctuation in gas mode is as small as in diesel mode. Therefore, the engine speed deviation is on a well acceptable level, comparable to the deviations in diesel mode [59]. Additional tests were done to study its performance under rough sea conditions. The first test covered a constant engine speed setpoint with torque fluctuations by means of a water brake. The second test done varying the engine speed setpoint. Both tests were successfully completed without knock or misfire. This means that the engine shows a good transient response behaviour and can therefore withstand to rough sea conditions in gas mode [59]. The definition of gas mode 99.5% natural gas and 0.5% diesel was checked with the author of the report [59]. It was confirmed that the amount of pilot fuel was not adjusted during the load response tests.

Based on engine manufacturer data from [59] a load response of 25% in 30 seconds (0.8% Pmax/s) can be achieved. This is however depended on the load and rotational speed. Building up the rotational speed from 25% to 70% can be done in less than a minute. Higher rotational speeds up to 100% require an additional 30 minutes. These capabilities are considered to be sufficient to operate properly within ports.

The natural gas (dual fuel) engine studied as reference used 0.5% pilot fuel applied in a prechamber resulting in a strong ignition source [59]. For ammonia hydrogen mixtures a sufficiently strong spark ignition system is to be developed. This could be realised by means of a spark plug in a prechamber with a rich fuel mixture igniting the rest of the lean fuel mixture in the cylinder. Such a method has already been applied in four-stroke pure gas engines [60]. This should be further investigated by an engine manufacturer.

5.2.4.2 Fuel supply

Besides the engine itself the fuel supply system also needs to be capable to cope with load changes. Therefore, a hydrogen and ammonia buffer tank could be installed preventing the need for more capacity of the cracker and evaporator to cope with load changes. This is something to be further investigated in a later design stage and out of the scope of this project.

5.2.5 Part load conditions

Based on engine manufacturer data from [59] the minimum engine power is approximately 5%. Furthermore, as an indication the minimum rotational speed is 25% (corresponding to 1-2% of engine power for the propeller). So, for slow speed the minimum engine power of 5% is the limiting factor. This results in a minimum sailing speed around 3-4 knots which is considered an acceptable speed in ports as mooring will be done with assistance of tugs.

5.2.6 Marine environment

Based on operational experience a slow speed two stroke engine is not significantly influenced by accelerations due to ship motions or salty air. Considering the fundamental design of the engine forces and impurities acting upon the engine have little to no effect on its operation. Changing the fuel type does not change the fundamental principles of the engine. Therefore, it is assumed that a slow speed two stroke engine using ammonia hydrogen mixtures is capable of handling accelerations and salty air without any necessary additions to or modifications of the power generation system. This should be further investigated by an engine manufacturer.

5.2.7 System efficiency

5.2.7.1 Engine

The total engine efficiency is the product of the thermal efficiency and the mechanical efficiency [61]. The thermal efficiency is depending on induced power, fuel consumption (mass flow) and the specific energy of the fuel [61]. The induced engine power is based on the same number of cylinders, stroke volume, mean effective pressure, rotational speed and stroke type. Using ammonia hydrogen mixtures instead of natural gas the induced power does not change. The fuel consumption in terms of mass flow does change as ammonia (as source for ammonia and hydrogen) has a lower specific energy. As discussed in 3.3 ammonia hydrogen mixtures can obtain similar properties as methane in both flame stability and flame speed. As mentioned in 4.4 natural gas is more than 90% (mol) methane. Therefore, it is expected that the energy consumption [kJ/kWh] of ammonia, providing ammonia hydrogen mixtures, is considered to be similar as natural gas. Combining that with the same induced engine power the thermal efficiency is assumed to be similar as well. The mechanical efficiency of the engine is assumed to be the same as there are no changes in the fundamental design of the engine that alter the mechanical design and operation. As both the thermal and mechanical efficiency are similar to natural gas the total engine efficiency is therefore also similar to natural gas.

Based on engine manufacturing data the total engine efficiency ranges between 49-52% depending on the point of operation. For this project a total engine efficiency of 50% is assumed.

The 50% efficiency is based on the usage of an ammonia hydrogen mixture. Converting this ammonia hydrogen mixture to pure ammonia consumption the efficiency is slightly increased, to 51.6%, as the losses in thermal energy are reused/added to crack the ammonia into hydrogen. See Table 5-4 for further explanation and Table 5-5 for the assumed ammonia hydrogen mixture.

	Total	Ammonia	Hydrogen	Cracking Ammonia	Efficiency [-]
Delivered [kW]	12,280	-	-	-	-
Consumed – engine [kW]	24,560	18,666	5,984	-	50.0%
Consumed – engine [kg/s]	-	1.004	0.049	-	-
Consumed – system [kg/s]	1.280	1.004	-	0.277	-
Consumed – system [kW]	23,811	18,666	-	5,146	51.6%
Added – cracking [kW]	749				-

Table 5-4: ICE efficiency clarification, ammonia hydrogen mixture translated in pure ammonia consumption

Mass [kg]		Volume [m3]		Energy [MJ]	
Ammonia	Hydrogen	Ammonia	Hydrogen	Ammonia	Hydrogen
95%	5%	70%	30%	76%	24%
0.54	0.03	0.70	0.30	10.01	3.24
0.57		1.00		13.25	

Table 5-5: Assumed ammonia hydrogen mixture, ICE option

5.2.7.2 Main engine support

To operate the engine multiple support systems are required such as cooling, lubrication, air and fuel supply. These systems consume energy and taken into account to calculate the actual efficiency of the engine delivering power to both the electrical and propulsion system. The demand of the engine support systems is estimated to be 3% of the total engine power.

5.2.7.3 Evaporator, Cracker and Tank heater

To calculate the energy demand for evaporation and partially cracking of the ammonia the following ammonia hydrogen mixture was assumed as per Table 5-5. This mixture composition has been applied in multiple researches and is considered to be the best first approximation in this project. This assumption has to further investigated by an engine manufacturer.

During continuous operation the available exhaust gas heat, which is assumed to be 30% of the energy put in the engine [61], is sufficient. The available exhaust gas heat 8.6 MW can evaporate the additional ammonia demand, as the boil off is insufficient for 100% Maximum Continuous Rating (MCR). In the worst case sailing back with only remaining cargo the boil off is very low, +/-0.03 vs +/-0.90 kg/s. Therefore, the evaporator demand and size are based on 0 boil-off condition, consuming 2.0 MW. In addition, the remaining available exhaust gas heat is sufficient to heat up and partially crack the ammonia, consuming 1.2 MW. The remainder of 5.4 MW exhaust gas heat is considered to be sufficient to cover the heat losses not taken into account in the calculation. See Appendix G for the entire calculation.

During start up the exhaust gas heat is not yet available therefore ammonia burners should be installed to heat up the system in the beginning. In addition, a hydrogen and ammonia buffer tank could supply the demand during start up.

With consuming more ammonia than the boil off the pressure in the storage tanks will drop. The pressure drop will increase the amount the boil off. However, the boil off could be insufficient to compensate for the lower pressure and temperature for a certain period of time. This could lead to a limit in the amount off ammonia which can be consumed. To compensate the lower pressure and temperature in the storage tank a heater can be applied. The heat can be gained from the cooling system of the main engine and regulated by a thermostatic valve to keep the storage tank on the correct temperature. For now, it is assumed that there is sufficient heat available in the main engine cooling system to keep the storage tank at the correct temperature. This is to be confirmed in a later design stage which is out of scope of this project.

The evaporator and cracker only consume fuel when starting up. During continuous operation the cracker and evaporator are provided with the required energy by means of exhaust gases and the tank heater by means of the cooling system of the main engine. Therefore, there no deduction is required on the system efficiency for these 3 components.

5.2.7.4 System

In design condition the goal is to deliver effective power to the propeller and the hotel load, combined 11,760 kW. To do so the main engine must also supply power to cover the main engine support systems, adding 430 kW. Including all losses in the supply of electrical energy the total makes 12,280 kW. The main engine efficiency is 51.6%, based on pure ammonia consumption resulting in an input demand of 23,798 kW. The system efficiency can therefore be calculated as 11,760 kW divided by the 23,798 kW, resulting in 49.4%.

5.2.8 Total cost of ownership

The total cost of ownership for the ICE option is calculated in two parts as shown in Table 5-6 and Table 5-7. As per assumptions explained in 5.1.8 and the results from this section so far, the following can be stated:

- Installed main engine: 14,310 kW
- Design point main engine: 12,280 kW
- Maximum ammonia input cracker: 0.355 kg/s (See Appendix G)
- Maximum ammonia input evaporator: 1.492 kg/s (See Appendix G)
- Main engine output: 79,820,000 kWh per year
- Main engine efficiency: 51.6% (based on ammonia consumption)
- Ammonia (fuel) consumption: 29,940 ton per year
- Effective cargo & less than base cargo, DWT: 50,533 & 1,565 ton (See Appendix H)
- DeNOx system is applied as NOx emissions are identified as per 5.2.3.1

Component	Figures	ΔCAPEX	Notes
*Main engine	400 €/kW	€5,724,000	Engine manufacturer guideline with added margin
Cracker	€115,000 per 50Nm ³ /hr -> 38.45 kg/hr -> 34x	€3,910,000	Equipment supplier guideline
Evaporator	€37,000 per 65.61 kg/hr -> 82x	€3,034,000	Equipment supplier guideline
DeNOx	40 €/kW	€572,400	Average of source: [62]
Total		€13,240,400	

Table 5-6: ΔCAPEX, ICE option

*including PTO – Shaft generator and AC/AC Frequency Converter

Component	Figures	ΔOPEX 1 year	ΔOPEX 25 years	Notes
*Main engine	2.5% CAPEX	€143,100	€3,577,500	Engine manufacturer guideline with added margin
Cracker	1.0% CAPEX	€39,100	€977,500	Estimation
Evaporator	1.0% CAPEX	€30,340	€758,500	Estimation
DeNOx	6 €/MWh	€478,920	€11,973,000	Average of source: [62] Running and maintenance cost
Fuel	850 €/ton	€25,449,000	€636,225,000	
Less income	581 €/ton	€909,801	€22,745,025	See Appendix H
Total		€27,050,261	€676,256,525	

Table 5-7: ΔOPEX, ICE option

*including PTO – Shaft generator and AC/AC Frequency Converter

This results in a ΔTCO of €689,496,925.

5.3 PEMFC

5.3.1 System definition

5.3.1.1 Propeller

Different than the internal combustion engine an electric motor is capable of operating on very low rotational speed and power levels. Therefore, an electric motor with an FPP has similar manoeuvrability properties as an electric motor with an CPP. As an FPP has a higher efficiency, as discussed in 5.2.1.2, than an CPP the FPP is selected for this option.

5.3.1.2 Electrical and Mechanical system

With this fuel cell option, the PEMFC provides electrical power for all systems onboard. Within the electrical system the power is converted and distributed accordingly. A fuel cell provides unregulated DC voltage which must first be converted to constant voltage by means of a converter before it can be used. Therefore, a DC/DC converter is applied directly after the PEMFC.

As most (fuel-)electric powered vessels use an AC switchboard and AC electric motors the system on likewise also setup with an AC switchboard and an AC electric motor. Therefore, a DC/AC inverter is applied after the DC/DC converter. The AC switchboard is used to distribute the electric power to the multiple consumers where depending on the type of load a transformer is used. Alternatively, it could be possible to obtain multiple voltage levels from the fuel cell stacks by specific arrangement of the power output preventing the need for a transformer. This could be further investigated. For now, it is assumed that all systems, except the electric motor, require a transformer. It is assumed that the fuel cell stacks are arranged in such a way that they can supply the electric motor with electrical power accordingly preventing the need of a transformer. This makes the system for the biggest consumer more efficient. The available electric power for the electric motor is regulated with a frequency converter so the entire range of speeds can be utilized.

Although efficiency is considered more important than power density the electric motor is connected to the propeller shaft by means of a gearbox. The power demand ranging from 4.5 to 11.5 MW already requires a large electric motor with gearbox. Removing the gearbox would result in a significant increase in size of the electric motor as the desired rotational speed for the propeller is +/-100 rpm. For this project it is considered that removing a gearbox is not possible as the size of the electric motor would result in serious undesirable design consequences. Reviewing the availability of electric motors with a power output of +/- 12 MW for marine applications rotational speeds are mostly above 1000 rpm confirming the need for a gearbox.

5.3.1.3 Overview

An overview of the design condition and distribution is given in Table 5-8. As only the design condition is investigated, as mentioned in 5.2.1.4, the bow thruster and re-liquefaction system is not further taken into account.

Load type	PEMFC		
	*Generated [kWe]	Delivered [kW]	Delivered [kWe]
Propeller shaft	12,849	11,500	
Purifier	**2.1% (thus: 276)		**2.0% (thus: 262)
Hotel	273		260
Bow thruster	***631		***600
Re-liquefaction	***1,104		***1,050

Table 5-8: Design condition and distribution, PEMFC option

*Efficiency of electrical system assumed as following:

DC/DC Converter: 99.0% [63]

DC/AC Inverter: 98.0% [64]

Switchboard (AC): 99.0% [50]

AC/AC Frequency Converter: 98.0% [49]

Electric motor: 96.0% [65]

Gearbox: 99.0% [12]

Transformer: 99.0% [50]

Total Propeller shaft: 89.5%

Total Hotel load/Purifier: 95.1%

** Estimation based on a reference of cracking and purification combined [36].

*** Only used in port if required.

Based on the provided data the design point of the PEMFC's is 13,398 kW. Assuming a power generation margin of 10%-15% the installed power is approximately 14,887kW-15,762 kW. For this project as reference 15,000kW of PEMFC's is selected.

The system design of the PEMFC is given in Figure 5-2.

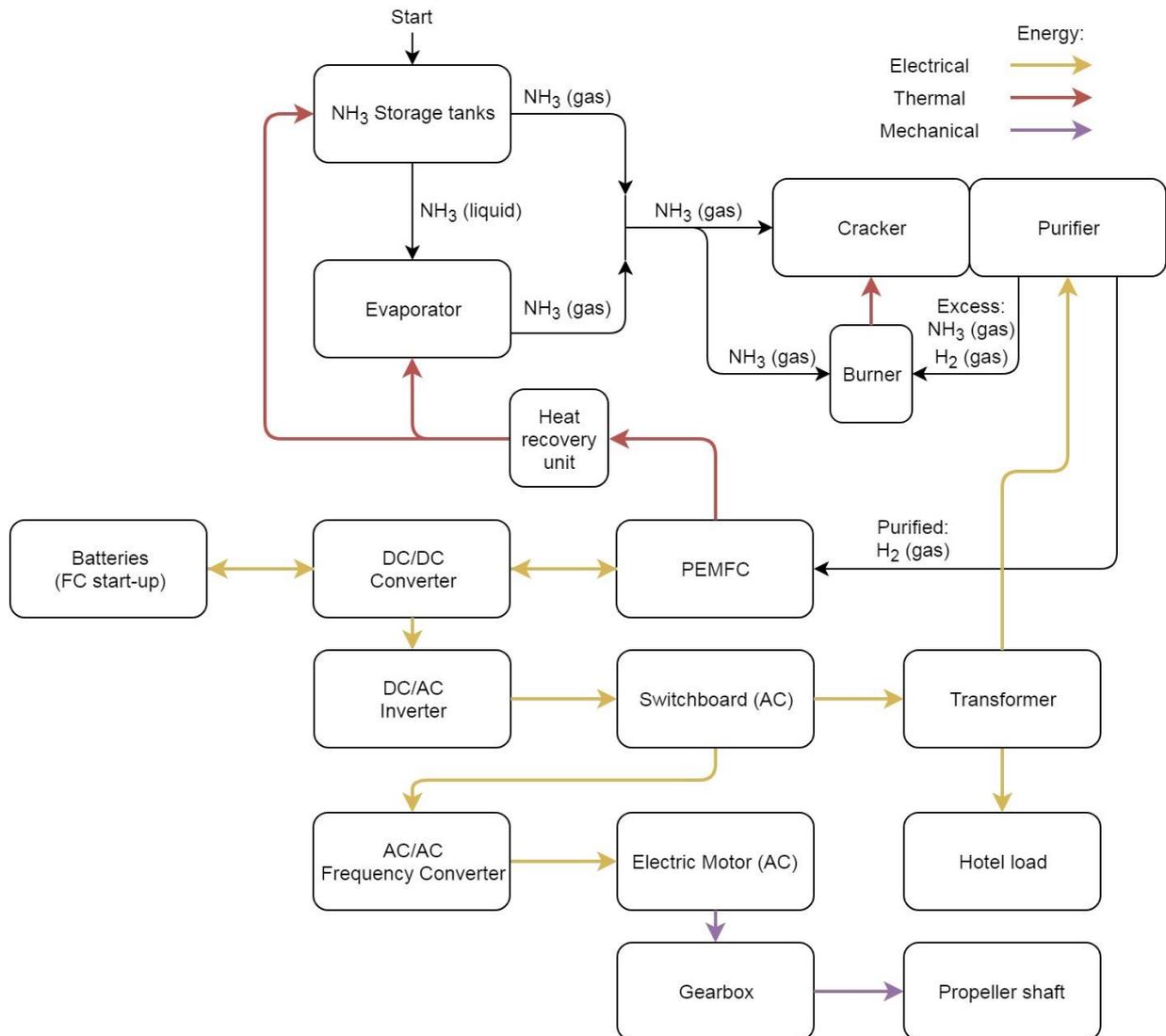


Figure 5-2: System design PEMFC option

5.3.2 Power density

Based on a 100kW PEMFC the power density can be determined by adding the fuel cell module with the coolant and air subsystem. Resulting in 256 kW/ton and 99 kW/m³. These figures are based on simplified measurements and are only used as guideline for comparison [32]. See Appendix I for the calculation.

5.3.3 Harmful emissions

5.3.3.1 NO_x

The PEMFC operates on low temperatures, ranging between 50 and 100°C [66], converting the chemical energy in hydrogen into electrical energy by through an electrochemical reaction of hydrogen with an oxidizing agent. During this process no conditions occur that produce NO_x [67]. Therefore, the NO_x emissions are 0 g/kWh. It is assumed that the burner continuously combusts ammonia under optimal conditions such that NO_x emissions are negligibly low.

5.3.3.2 Fuel slip

The excess ammonia and hydrogen from the cracker and purifier are used in the burner. It is assumed that the continuous operation of the burner all supplied fuel is combusted. Therefore, no fuel slip is identified in this system. With the cracker, purifier, burner and PEMFC not emitting any harmful emissions no harmful emissions are identified in this system.

5.3.4 Load response

5.3.4.1 PEMFC & Electric motor

As discussed in 3.5.1 PEMFC's are used in multiple mobile applications. Considering load response, the PEMFC can be designed in such a way it can accommodate the load response demands of cars and buses capable to go from 10% to 90% power in a few seconds. As indication this would be at least 16% Pmax/s.

Considering the primary use, to power the electric motor, the PEMFC is considered to have more than sufficient load response capability to cope with fluctuating demands of heavy weather conditions and ramping up and down in port areas.

A PEMFC can be tailor made, for instance the load response can be tuned down making it less complex and cheaper. If needed the batteries used for start-up power for the fuel cell could also be used for peak shaving covering the demand for load response.

Based on the working principle [12] confirmed by operational experience the electric motor for marine propulsion has shown to have adequate load response characteristics. Fluctuating loads during heavy weather conditions mostly result in fluctuating electric power demands and keeping the rotational speed within an acceptable range.

5.3.4.2 Fuel supply

As discussed in 5.2.4.2 a buffer tank might be required to cope with high fluctuating loads. A buffer tank can prevent the need for more capacity of the cracker, purifier and evaporator. This is something to be further investigated in a later design stage and out of the scope of this project.

5.3.5 Part load conditions

As a single fuel cell is 100 kW multiple fuel cells will have to be installed. The idle power of a PEMFC is approximately 6% [32]. So, for all fuel cells in operation 6% of the total power is a minimum. However, this can easily be lowered by turning multiple fuel cells off and limit the use to just a couple. With this capability the required minimum output for slow speeds in port areas can easily be achieved.

5.3.6 Marine environment

Since PEMFC's are already applied in various mobile applications, like cars and busses, PEMFC's have shown to be capable of handling forces due to accelerations. Therefore, it is not expected that accelerations experienced onboard a vessel will cause a problem for PEMFC's.

As PEMFC's are sensitive to several types of contamination [68] salty air and other air pollutants could reduce the performance over time. Therefore, it is considered that air treatment in the form of filtration is required in the air supply of the PEMFC's. The extend of air filtration is out of scope of this project and should be investigated further.

5.3.7 System efficiency

5.3.7.1 PEMFC

The efficiency of a PEMFC currently varies between 50% and 60% [30]. For this project an efficiency of 55% is assumed for the PEMFC using hydrogen. This efficiency already includes the demand of the coolant and air subsystems. The precise efficiency is to be further investigated in a later design stage if a PEMFC is selected for power generation onboard.

Likewise, with the ICE the input of hydrogen needs to be converted into ammonia for fair comparison. See Table 5-9 for clarification.

	Total	Hydrogen	Cracking Ammonia	Efficiency [-]
Delivered [kW]	13,398	-	-	-
Consumed – PEMFC [kW]	24,360	24,360	-	55.0%
Consumed – PEMFC [kg/s]	0.203	0.203	-	-
Consumed – system [kg/s]	1.143	-	1.143	-
Consumed – system [kW]	21,267	-	21,267	63.0%
Added – cracking [kW]	3,093	-	-	-

Table 5-9: PEMFC efficiency clarification, hydrogen translated in ammonia consumption

5.3.7.2 Cracker and Purifier

The cracker is supplied with heat from the burner. The burner consumes 5,144 kW ammonia to heat up and crack the ammonia, see Appendix J for the calculation. To maintain the proper flow and pressure the purifier consumes approximately 2% of the provided electrical power from the PEMFC's, 276 kWe of generated power (thus 262 kWe delivered power). This is an estimation based on a reference of cracking and purification combined [36].

5.3.7.3 Evaporator and Tank heater

Likewise, with the ICE the cooling system of the PEMFC can be utilized to supply heat to both the evaporator and the tank heater. The available power in heat is in a similar range as the ICE yet the temperatures are lower. Therefore, the available heat can only be utilized for evaporation and tank heating and not for cracking. Since the available heat is only used for the evaporator and tank heater it is considered to be sufficient without additional electrical power, as the available heat and demand calculation has already been made for the ICE indicating sufficient overcapacity.

5.3.7.4 System

In design condition the goal is to deliver effective power to the propeller and the hotel load, combined 11,760 kW. To do so the PEMFC's must supply power to the electrical system covering the propeller 12,849 kW, hotel load 273 kW and 276 kW for the purifier making a total of 13,398 kW. The PEMFC efficiency is 63% based on ammonia consumption resulting in an input demand for the PEMFC's of 21,267 kW. In addition, the burner consumes 5,144 kW of ammonia making a total of 26,411 kW. This leads to an ammonia conversion efficiency of 13,398 kW divided by 26,411 kW, resulting in 50.7%. The system efficiency can therefore be calculated as 11,760 kW divided by the 26,411 kW, resulting in 44.5%.

5.3.8 Total cost of ownership

The total cost of ownership for the PEMFC option is calculated in two parts as shown in Table 5-10 and Table 5-11. As per assumptions explained in 5.1.8 and the results from this section so far, the following can be stated:

- Installed PEMFC's: 15,000 kW
- Design point PEMFC's: 13,398kW
- Installed electric motor: 13,000 kW
- Maximum ammonia input cracker: 1.280 kg/s (See Appendix J)
- Maximum ammonia input evaporator: 1.590 kg/s (See Appendix J)
- PEMFC efficiency: 63.0% (based on ammonia consumption)
- PEMFC incl. burner efficiency: 50.7% (based on ammonia consumption)
- PEMFC's output: 87,087,000 kWh per year
- Ammonia (PEMFC+burner) consumption: 26,755 + 6,491 = 33,246 ton per year
- Effective cargo & less than base cargo, DWT: 50,184 & 1,915 ton (See Appendix H)

Component	Figures	ΔCAPEX	Notes
PEMFC's	800 €/kW	€12,000,000	Fuel cell manufacturer guideline
Cracker incl. Burner & Purifier	€150,000 per 50Nm ³ /hr -> 38.45 kg/hr -> 120x	€18,000,000	Equipment supplier guideline with added margin for purifier
Evaporator	€37,000 per 65.61 kg/hr -> 88x	€3,256,000	Equipment supplier guideline
*Additional electrical systems	500 €/kW	€7,500,000	Estimation
Electric motor	250 €/kW	€3,250,000	Estimation
Gearbox	50 €/kg, 2 kg/kW	€1,300,000	Estimation
Total		€45,306,000	

Table 5-10: ΔCAPEX, PEMFC option

Component	Figures	ΔOPEX 1 year	ΔOPEX 25 years	Notes
PEMFC	2.5% CAPEX	€300,000	€7,500,000	Estimation
Cracker incl. Burner & Purifier	1.0% CAPEX	€180,000	€4,500,000	Estimation
Evaporator	1.0% CAPEX	€32,560	€814,000	Estimation
*Additional electrical systems	1.0% CAPEX	€75,000	€1,875,000	Estimation
Electric motor	1.0% CAPEX	€32,500	€812,500	Estimation
Gearbox	2.5% CAPEX	€32,500	€812,500	Estimation
Fuel	850 €/ton	€28,259,100	€706,477,500	
Less income	581 €/ton	€1,113,040	€27,826,000	See Appendix H
Total		€30,024,700	€750,617,500	

Table 5-11: ΔOPEX, PEMFC option

*Covers: DC/DC Converter, DC/AC Inverter, additional Switchboards, additional Transformers and AC/AC Frequency Converter

This results in a ΔTCO of €795,923,500.

5.4 AFC

5.4.1 System definition

Likewise, with the PEMFC as discussed in 5.3.1 the same design principle is applied for the AFC.

An overview of the design condition and distribution is given in Table 5-12. As only the design condition is investigated, as mentioned in 5.2.1.4, the bow thruster and re-liquefaction system is not further taken into account.

Load type	AFC		
	*Generated [kWe]	Delivered [kW]	Delivered [kWe]
Propeller shaft	12,849	11,500	
Hotel	273		260
Bow thruster	**631		**600
Re-liquefaction	**1,104		**1,050

Table 5-12: Design condition and distribution, AFC option

*Efficiency of electrical system assumed as following:

DC/DC Converter: 99.0% [63]

DC/AC Inverter: 98.0% [64]

Switchboard (AC): 99.0% [50]

AC/AC Frequency Converter: 98.0% [49]

Electric motor: 96.0% [65]

Gearbox: 99.0% [12]

Transformer: 99.0% [50]

Total Propeller shaft: 89.5%

Total Hotel load/Cracker & purifier: 95.1%

**Only used in port if required.

Based on the provided data the design point of the AFC's is 13,122 kW. Assuming a power generation margin of 10%-15% the installed power is approximately 14,580kW-15,438 kW. For this project as reference 15,000kW of AFC's is selected.

The system design of the AFC is given in Figure 5-3.

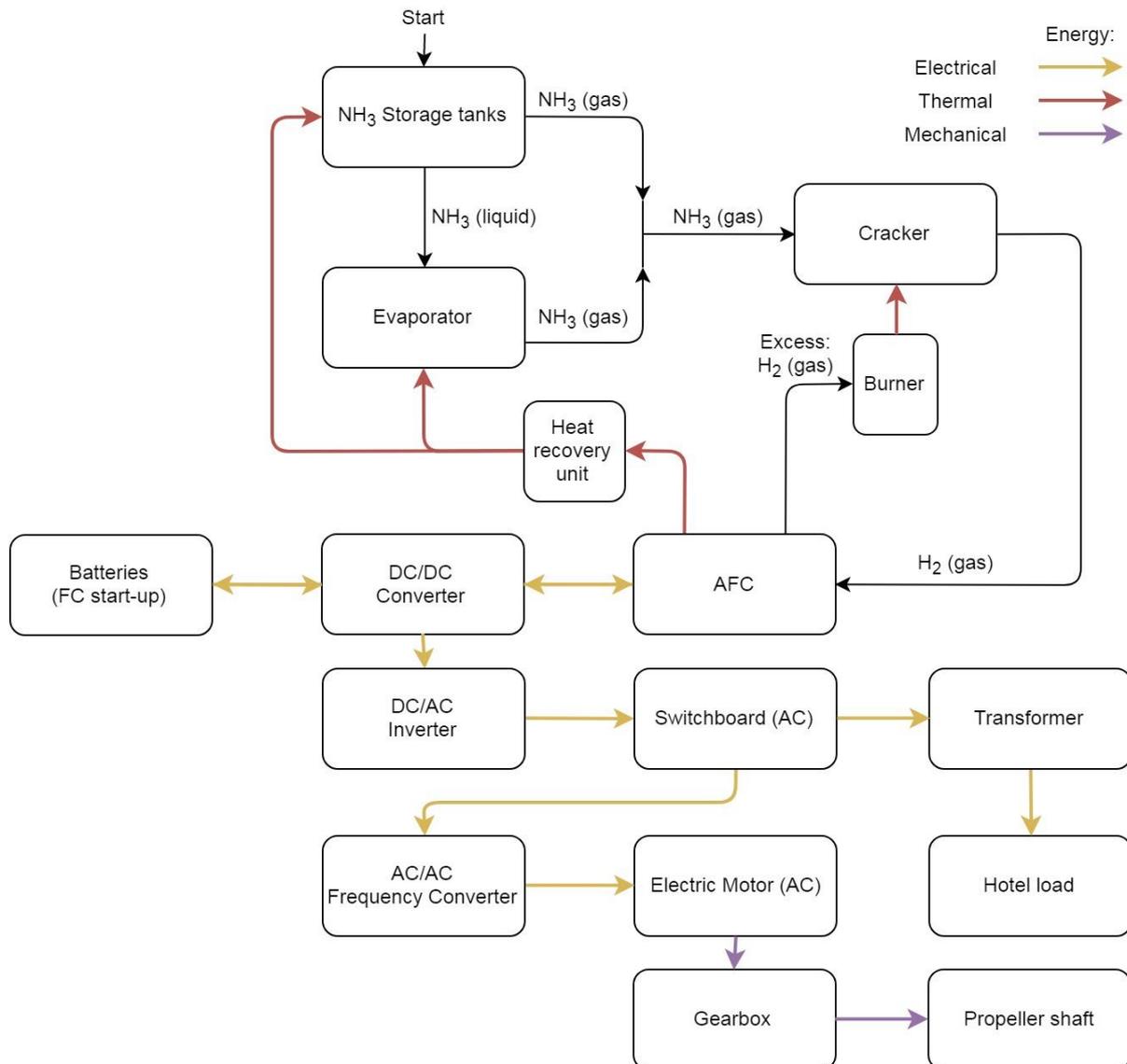


Figure 5-3: System design AFC option

5.4.2 Power density

Based on a 4kW AFC [37] the power density is determined by estimating the actual size of the fuel cell module. Resulting in 8 kW/ton and 6 kW/m³. These figures are based on simplified measurements and are only used as guideline for comparison. See Appendix K for the calculation.

5.4.3 Harmful emissions

5.4.3.1 NO_x

Likewise, with the PEMFC the AFC also operates on low temperatures [39]. Furthermore, it works on a similar principle as the PEMFC thus the AFC does not emit NO_x emissions. It is assumed that the burner continuously combusts ammonia under optimal conditions such that NO_x emissions are negligible low.

5.4.3.2 Fuel slip

The excess hydrogen and small amount of uncracked ammonia from the AFC are used in the burner. It is assumed that the continuous operation of the burner all supplied fuel is combusted. Therefore, no fuel slip is identified in this system.

5.4.4 Load response

Although the AFC has not been adopted as widely in transportation as the PEMFC both technologies have been found to be sufficiently fast for automotive applications when oxygen is used as cathode gas [69]. As discussed earlier in 5.3.4 accommodating the load response demands of cars and buses corresponds to capability going from 10% to 90% power in a few seconds. As indication this would be at least 16% P_{max}/s . The research into the dynamic behaviour of the AFC [69] did use pure oxygen which is different from different regular air. The effects of air as an oxidizing agent rather than pure oxygen for the dynamic behaviour of the AFC are unknown. For now, it is assumed that load response of the AFC is at least 16% P_{max}/s . This should be further investigated in a different study.

5.4.5 Part load conditions

Likewise, with the PEMFC the AFC will make use of multiple small fuel cells. This makes the idle power of a single fuel cell less relevant as the minimum output for slow speeds in port areas can be achieved by turning off multiple fuel cells.

5.4.6 Marine environment

Likewise, with the PEMFC the AFC has also been proposed as option for the automotive industry [70]. Furthermore, the AFC has been successfully applied in several space programs [71]. Therefore, it is concluded that the AFC is sufficiently capable to cope with the accelerations experienced onboard vessels.

Considering the sensitivity of the AFC CO_2 poisoning is a major concern [30]. Therefore, air treatment in the form of CO_2 scrubbing is required. To what extend additional air treatment is required in unknown and should be further investigated. For now, it is assumed that only air treatment in the form of CO_2 scrubbing is required.

5.4.7 System efficiency

5.4.7.1 AFC & Cracker

According to earlier market research the efficiency of an AFC currently varies between 50% and 60% [30]. Based on experimental research for this particular setup, as shown in Figure 5-3, a gross electrical efficiency of AFC with cracker, thus including burner, of 59% can be achieved [39] based on ammonia consumption. Deducting the 59% for the required subsystems, cooling and air supply, within the fuel cell by 15% based on a fuel cell manufacturer guideline the resulting efficiency is 50%. For this project an efficiency of AFC with cracker, including burner of 50% is assumed. An AFC manufacturer [37] which uses a similar operating principle claims an efficiency of 52% confirming that 50% is not an unrealistic figure.

5.4.7.2 Evaporator & Tank heater

Likewise, with the ICE the cooling system of the AFC can be utilized to supply heat to both the evaporator and the tank heater. The available power in heat is in a similar range as the ICE yet the temperatures are lower. Therefore, the available heat can only be utilized for evaporation and tank heating and not for cracking. Since the available heat is only used for the evaporator and tank heater it is considered to be sufficient without additional electrical power, as the available heat and demand calculation has already been made for the ICE indicating sufficient overcapacity.

5.4.7.3 System

In design condition the goal is to deliver effective power to the propeller and the hotel load, combined 11,760 kW. To do so the AFC's must supply power to the electrical system covering the propeller 12,849 kW, hotel load 273 kW making a total of 13,122 kW. The AFC efficiency is 50% resulting in an

input demand of 26,244 kW. The system efficiency can therefore be calculated as 11,760 kW divided by the 26,244 kW, resulting in 44.8%.

5.4.8 Total cost of ownership

The total cost of ownership for the AFC option is calculated in two parts as shown in Table 5-13 and Table 5-14. As per assumptions explained in 5.1.8 and the results from this section so far, the following can be stated:

- Installed AFC's: 15,000 kW
- Design point AFC's: 13,122kW
- Installed electric motor: 13,000 kW
- Maximum ammonia input cracker: 1.613 kg/s (See Appendix L)
- Maximum ammonia input evaporator: 1.613 kg/s (See Appendix L)
- AFC efficiency: 50% (based on ammonia consumption)
- AFC's output: 85,293,000 kWh per year
- Ammonia (fuel) consumption: 33,017 ton per year
- Effective cargo & less than base cargo, DWT: 50,208 & 1,891 ton (See Appendix H)

Component	Figures	ΔCAPEX	Notes
AFC's	2,000 €/kW	€30,000,000	Estimation
Cracker incl. Burner	€115,000 per 50Nm ³ /hr -> 38.45 kg/hr -> 152x	€17,480,000	Equipment supplier guideline
Evaporator	€37,000 per 65.61 kg/hr -> 89x	€3,293,000	Equipment supplier guideline
*Additional electrical systems	500 €/kW	€7,500,000	Estimation
Electric motor	250 €/kW	€3,250,000	Estimation
Gearbox	50 €/kg, 2 kg/kW	€1,300,000	Estimation
Total		€62,823,000	

Table 5-13: ΔCAPEX, AFC option

Component	Figures	ΔOPEX 1 year	ΔOPEX 25 years	Notes
AFC's	2.5% CAPEX	€300,000	€7,500,000	Estimation
Cracker incl. Burner	1.0% CAPEX	€174,800	€4,370,000	Estimation
Evaporator	1.0% CAPEX	€32,930	€823,250	Estimation
*Additional electrical systems	1.0% CAPEX	€75,000	€1,875,000	Estimation
Electric motor	1.0% CAPEX	€32,500	€812,500	Estimation
Gearbox	2.5% CAPEX	€32,500	€812,500	Estimation
Fuel	850 €/ton	€28,064,450	€701,611,250	
Less income	581 €/ton	€1,098,960	€27,474,000	See Appendix H
Total		€29,802,140	€745,053,500	

Table 5-14: ΔOPEX, AFC option

*Covers: DC/DC Converter, DC/AC Inverter, additional Switchboards, additional Transformers and AC/AC Frequency Converter

This results in a Δ TCO of €807,876,500.

5.5 SOFC

5.5.1 System definition

Similar to both PEMFC and AFC the SOFC uses the same design principle for the power generation system.

An overview of the design condition and distribution is given in Table 5-15. As only the design condition is investigated, as mentioned in 5.2.1.4, the bow thruster and re-liquefaction system is not further taken into account.

Load type	SOFC		
	*Generated [kWe]	Delivered [kW]	Delivered [kWe]
Propeller shaft	12,849	11,500	
Hotel	273		260
Bow thruster	**631		**600
Re-liquefaction	**1,104		**1,050

Table 5-15: Design condition and distribution, SOFC option

*Efficiency of electrical system assumed as following:

DC/DC Converter: 99.0% [63]

DC/AC Inverter: 98.0% [64]

Switchboard (AC): 99.0% [50]

AC/AC Frequency Converter: 98.0% [49]

Electric motor: 96.0% [65]

Gearbox: 99.0% [12]

Transformer: 99.0% [50]

Total Propeller shaft: 89.5%

Total Hotel load/Cracker & purifier: 95.1%

**Only used in port if required.

Based on the provided data the design point of the SOFC's are 13,122 kW. Assuming a power generation margin of 10%-15% the installed power is approximately 14,580kW-15,438 kW. For this project as reference 15,000kW of SOFC's is selected.

The system design of the SOFC is given in Figure 5-4.

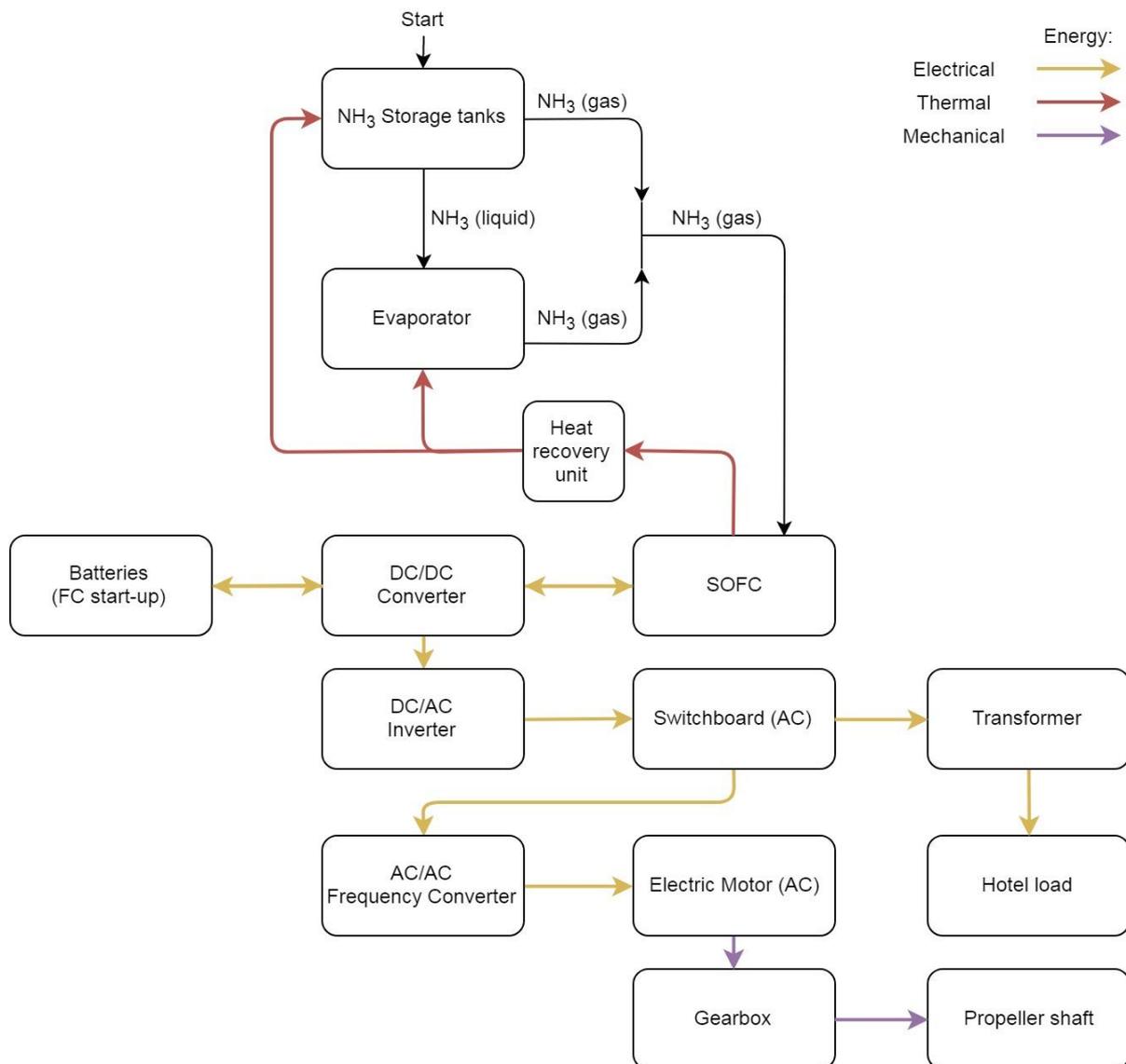


Figure 5-4: System design SOFC option

5.5.2 Power density

Based on a 1.5kW (AC output) SOFC [72] the power density is determined by estimating the actual size of the fuel cell module plus the cooling and air supply subsystem. The reference fuel cell system also includes a DC/DC converter, DC/AC inverter and other miscellaneous equipment. Therefore, the power density is based on an estimated 50% of the given size and mass. Furthermore, the DC power output, 1.67 kW [72] is used. Resulting in 17 kW/ton and 8 kW/m³. These figures are based on simplified measurements and are only used as guideline for comparison. See Appendix M for the calculation.

5.5.3 Harmful emissions

5.5.3.1 NO_x

The SOFC has an operating temperature of approximately 800 °C. Although this is higher than the PEMFC and AFC research [40] has shown that formation of NO_x can still be prevented.

5.5.3.2 Fuel slip

The operating temperature causes the ammonia to decompose inside the SOFC. Considering this temperature and with sufficient air supply the fuel slip, both ammonia and hydrogen is expected to be minimal based on its principal design. Therefore, the remaining fuel slip is considered low enough that it can easily dissolve in water, which is created in the SOFC, to none harmful concentrations. This should be further investigated in a later design stage.

5.5.4 Load response

Research looking into the dynamic behaviour of the SOFC [73] clearly showed that the electrochemical response is adequate, but the major part of the complete response is slow due to the thermal response. Based on that research an average is taken to be 0.003 %Pmax/s. This value is only obtained as guideline for comparison only.

Besides the load response while active the start-up time is also relevant for the SOFC. Assuming a ramp up rate, for starting the SOFC, of 2°C/min [74] [75] with an operating temperature of approximately 800°C, the start-up time is multiple hours. This might be an additional challenge for load response as not all SOFC's might be in operation.

5.5.5 Part load conditions

Likewise, with the PEMFC the SOFC will make use of multiple small fuel cells. This makes the idle power of a single fuel cell less relevant as the minimum output for slow speeds in port areas can be achieved by turning off multiple fuel cells. However, the number of fuel cells that are turned off have influence on the general load response as the start-up time is significant. Therefore, to limit the impact on general load response the capability of idle power should be further investigated.

5.5.6 Marine environment

The SOFC compared to the PEMFC and AFC is clearly less sensitive to impurities [30]. An SOFC stack has already been tested on multiple vessels. One of them was the Viking Lady where successful operation was achieved in offshore conditions. Therefore, it is concluded that both accelerations and salty air are no serious issue for the SOFC.

5.5.7 System efficiency

5.5.7.1 SOFC

According to earlier market research the efficiency of a SOFC currently varies between 50% and 60% [30]. However, efficiencies above 60% have also been reached [40]. For this project an efficiency of 60% is assumed. This efficiency already includes the demand of the coolant and air subsystems. The precise efficiency is to be further investigated in a later design stage if a SOFC is selected for power generation onboard.

5.5.7.2 Evaporator and Tank heater

Likewise, with the ICE the cooling system of the SOFC can be utilized to supply heat to both the evaporator and the tank heater. The available power in heat is in a similar range as the ICE. Since the available heat is only used for the evaporator and tank heater it is considered to be sufficient without additional electrical power, as the available heat and demand calculation has already been made for the ICE indicating sufficient overcapacity.

5.5.7.3 System

In design condition the goal is to deliver effective power to the propeller and the hotel load, combined 11,760 kW. To do so the SOFC's must supply power to the electrical system covering the propeller

12,849kW and hotel load 273 kW making a total of 13,122 kW. The SOFC efficiency is 60% resulting in an input demand of 21,870 kW. The system efficiency can therefore be calculated as 11,760 kW divided by the 21,870 kW, resulting in 53.8%.

5.5.8 Total cost of ownership

The total cost of ownership for the SOFC option is calculated in two parts as shown in Table 5-16 and Table 5-17. As per assumptions explained in 5.1.8 and the results from this section so far, the following can be stated:

- Installed SOFC's: 15,000 kW
- Design point SOFC's: 13,122 kW
- Installed electric motor: 13,000 kW
- Maximum ammonia input evaporator: 1.344 kg/s (See Appendix N)
- SOFC's output: 85,293,000 kWh per year
- SOFC efficiency: 60% (based on ammonia consumption)
- Ammonia consumption: 27,514 ton per year
- Effective cargo & less than base cargo, DWT: 50,790 & 1,309 ton (See Appendix H)

Component	Figures	ΔCAPEX	Notes
SOFC's	5,000 €/kW	€75,000,000	Fuel cell manufacturer guideline [76]
Evaporator	€37,000 per 65.61 kg/hr -> 74x	€2,664,000	Equipment supplier guideline
*Additional electrical systems	500 €/kW	€7,500,000	Estimation
Electric motor	250 €/kW	€3,250,000	Estimation
Gearbox	50 €/kg, 2 kg/kW	€1,300,000	Estimation
Total		€89,714,000	

Table 5-16: ΔCAPEX, SOFC option

Component	Figures	ΔOPEX 1 year	ΔOPEX 25 years	Notes
SOFC's	2.5% CAPEX	€1,875,000	€46,875,000	Estimation
Evaporator	1% CAPEX	€26,640	€666,000	Estimation
*Additional electrical systems	1% CAPEX	€75,000	€1,875,000	Estimation
Electric motor	1% CAPEX	€32,500	€812,500	Estimation
Gearbox	2.5% CAPEX	€32,500	€812,500	Estimation
Fuel	850 €/ton	€23,386,900	€584,672,500	
Less income	581 €/ton	€760,639	€19,015,975	See Appendix H
Total		€26,189,179	€654,729,475	

Table 5-17: ΔOPEX, SOFC option

*Covers: DC/DC Converter, DC/AC Inverter, additional Switchboards, additional Transformers and AC/AC Frequency Converter

This results in a ΔTCO of €744,443,475.

5.6 Comparison of Options

As a summary of this chapter all four options are compared and listed in Table 5-18, Table 5-19 and Figure 5-5.

Option	*Power density		Harmful emissions	***Load response		
	[kW/ton]	[kW/m ³]		Heavy weather	Port	[%Pmax/s]
ICE	+/-38	+/-29	**+/-14 g/kWh NOx & 100ppm ammonia slip	V	V	+/-0.800
PEMFC	+/-256	+/-99	None	V	V	>16.000
AFC	+/-8	+/-6	None	V	V	>16.000
SOFC	+/-17	+/-8	None	X	X	+/-0.003

Table 5-18: Comparison of options, Part 1

*Power density is a guideline based on simplified measurements of the engine or fuel cell only. Other equipment such as support systems and electrical systems are excluded.

**Emissions of main engine, apply SCR to reduce NOx as much as possible.

***Load response:

V: System has sufficient capability to cope with conditions

X: System insufficiently capable, additional measures to be taken, part of problem could be solved with batteries, which are already installed for start-up power

%Pmax/s is a guideline only.

Option	*Part load	Marine environment	System efficiency	Total cost of ownership (ΔTCO)
ICE	V	No issues	49.4%	€689,496,925
PEMFC	V	Air treatment required: filtration	44.5%	€795,923,500
AFC	V	Air treatment required: CO ₂ scrubbing	44.8%	€807,876,500
SOFC	V	No issues	53.9%	€744,443,475

Table 5-19: Comparison of options, Part 2

*Part load

V: System has sufficient capability to supply minimum power in port conditions

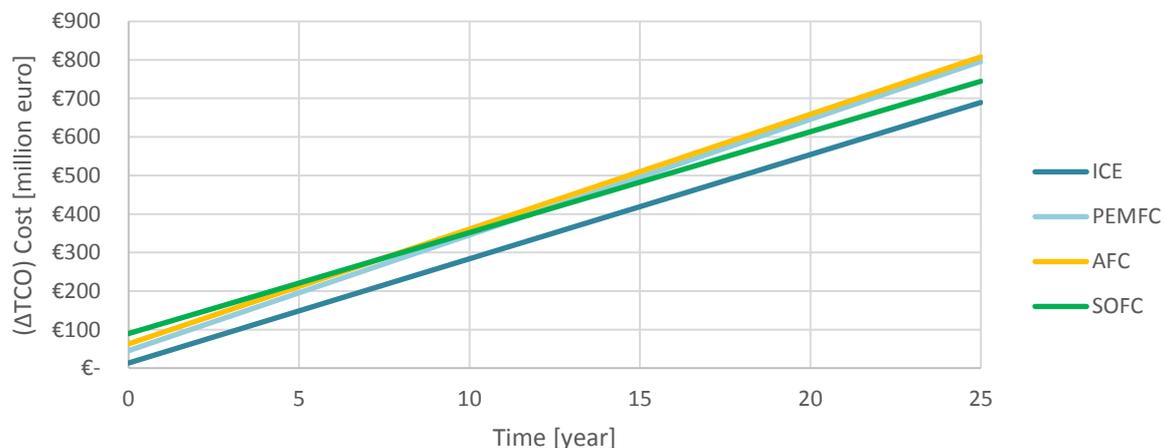


Figure 5-5: Cost comparison of options

Reviewing the comparison, the SOFC is clearly the most efficient. However, it does have practical challenges as the power density and load response capability are not on an acceptable level yet. Furthermore, despite the higher efficiency of the SOFC the total cost of ownership (Δ TCO) is still higher than the ICE based on these guidelines and estimations. The SOFC has a significant higher Δ CAPEX than the ICE. This makes ship owners more reluctant to adopt this technology as the savings in Δ OPEX could still take too long, which is a risk not taken often. The purchase and maintenance cost of the SOFC should be further investigated to obtain more accurate analysis.

The (two-stroke low speed) internal combustion engine is second in efficiency and therefore more efficient than the PEMFC and the AFC. Furthermore, the ICE is less expensive, more robust and has acceptable power density and load response capability.

5.7 Conclusion

Based on the comparison the ICE is selected as best option as it has high efficiency and is sufficiently practical. In the future further development of fuel cell technology might change this evaluation. An outlook and recommendations are given at the end of chapter 6. The selected option, the ICE is shown in Figure 5-6.

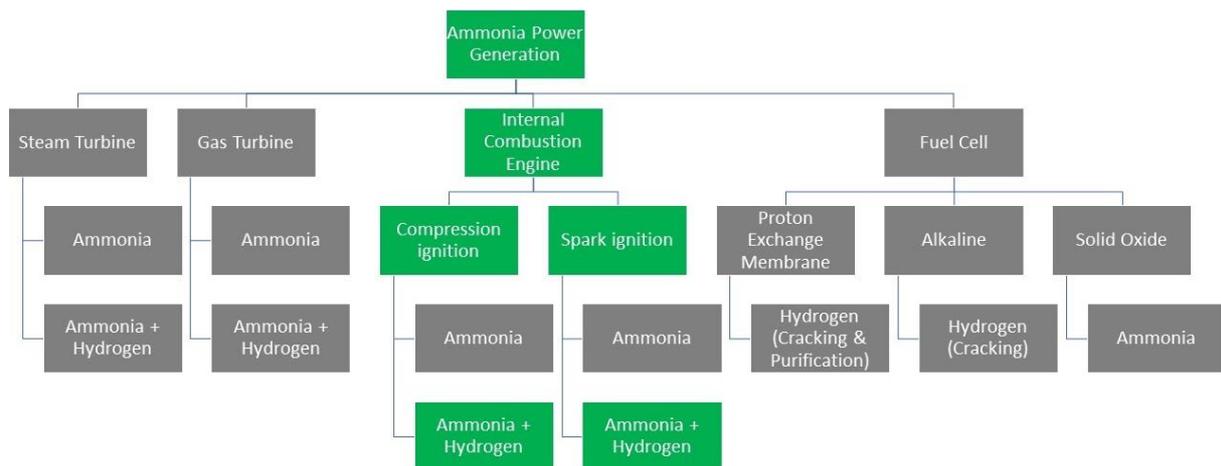


Figure 5-6: Ammonia power generation: Selection of marine performance options

6 AMMONIA PERFORMANCE COMPARISON WITH CONVENTIONAL POWER GENERATION

In this chapter the selected ammonia powered option, the ICE, will be compared to the conventional option. The comparison will cover both technical and economic performance. Furthermore, besides the conclusion an outlook and recommendation will be given at the end of this chapter.

6.1 Conventional Option

6.1.1 System definition

The conventional option is based on the same design principles as discussed in 5.2. However, as the conventional option operates on Heavy Fuel Oil (HFO), the boil off needs to be re-liquified. Therefore, re-liquification power demand is included in the design condition and thus the main engine size. An overview of the design condition and distribution is given in Table 6-1. As mentioned in 5.2 generators and systems not covered by the main engine are not included as they are out of scope.

Load type	Main engine		***Generators [kWe]
	Propeller shaft [kW]	PTO – *Delivered [kW] – [kWe]	
Propeller shaft	11,500		
Main engine support		554 – 490	
Hotel		**294 – 260	**260
Bow thruster			****600
Re-liquefaction		**1,188 – 1,050	**1,050

Table 6-1: Design condition and distribution, Conventional option

*Efficiency of electrical system assumed as following:

PTO – Shaft generator efficiency: 92.0% [48]

AC/AC Frequency Converter: 98.0% [49]

Switchboard (AC): 99.0% [50]

Transformer: 99.0% [50]

Total: 88.4%

**In transit covered by main engine, in port covered by generators.

***Losses due to switchboard and transformer to be in cooperated.

****Only used in port if required.

Based on the provided data the design point of the engine is 13,536 kW with cargo, and 12,348 kW without cargo. Assuming an engine margin of 10%-15%, based on the condition with cargo, the installed power is approximately 15,040 kW-15,925 kW. For this project as reference a MAN G60ME 16,080 kW (6 cylinders) is selected.

The system design of the internal combustion engine option is given in Figure 6-1. As mentioned in 5.2 operation in and around ports or any other condition a generator might be required is out of the scope of this project.

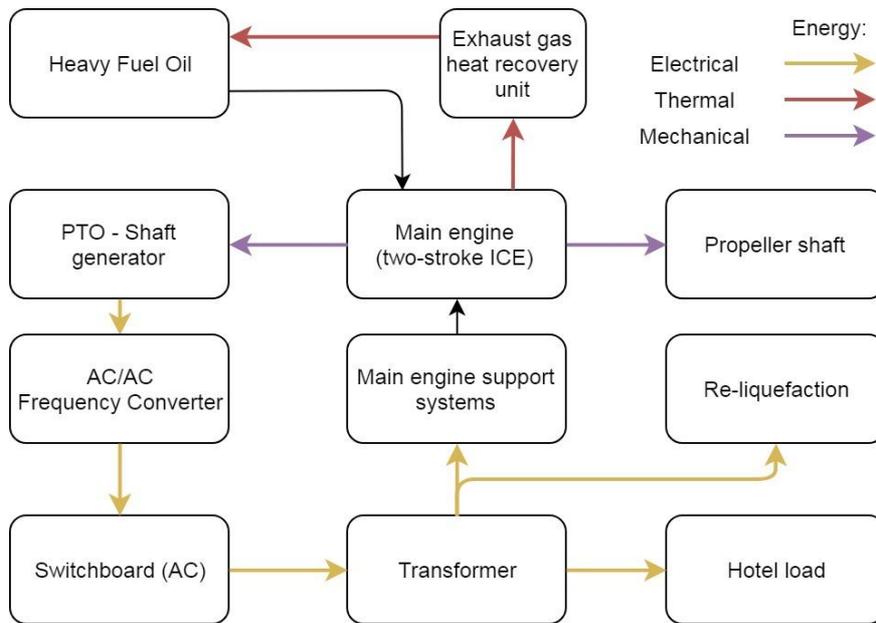


Figure 6-1: System design Conventional option

6.1.2 Power density

Based on the conventional engine for the 54,000 ton DWT ammonia carrier the resulting power density is 35 kW/ton and 32 kW/m³. These figures are based on simplified measurements and are only used as guideline for comparison [7]. See Appendix O for the calculation.

6.1.3 Harmful emissions

Based on an operating efficiency of the main engine of 50%, which will be clarified in 6.1.7.1, the emissions can be identified with combustion of HFO as per Table 6-2. The 50% efficiency can be expressed in 7200 kJ/kWh, assuming 40,000 kJ/kg for low sulphur 0.5% HFO this results in 180 g/kWh fuel consumption.

Harmful Emission	Figures	Result [g/kWh]	Notes
CO ₂	3.114 g/g-fuel [77]	561	-
SO _x & PM	0.5% = 0.005 g/g-fuel	1	Sulphur Cap 2020 [46]
NO _x	-	14	IMO Tier II [46]

Table 6-2: Harmful emissions Conventional option

6.1.4 Load response

Based on operational experience in the maritime industry the load response of a diesel engine can be considered adequality sufficient to cope with both heavy weather and port conditions.

6.1.5 Part load conditions

Based on operational experience in the maritime industry a diesel engine can be considered adequality capable to supply a minimum power so acceptable low speeds in port can be achieved.

6.1.6 Marine environment

Based on operational experience in the maritime industry a diesel engine can be considered adequality capable to cope with both accelerations and salty air.

6.1.7 System efficiency

6.1.7.1 Main engine

A slow speed two-stroke diesel engine has similar efficiency ranges as what has been discussed in 5.2.7.1 [7]. Therefore, for this project it is assumed the main engine has an efficiency of 50%.

6.1.7.2 Main engine support systems

The same estimation of 3% of the total engine power, as mentioned in 5.2.7.2, is used for the conventional option. Additional power demand for fuel oil heating is assumed to be covered by the excess of thermal energy of the main engine.

6.1.7.3 System

In design condition, when full, the goal is to deliver effective power to the propeller the hotel load and ammonia re-liquification plant, combined 12,810 kW. To do so the main engine must also supply power to cover the main engine support systems, adding 490 kW. Including all losses in the supply of electrical energy the total makes 13,536 kW. The main engine efficiency is 50% resulting in an input demand of 27,072 kW. The system efficiency can therefore be calculated as 12,810 kW divided by the 27,072 kW, resulting in 47.3%.

6.1.8 Total cost of ownership

The total cost of ownership (Δ TCO) for the conventional option is calculated in two parts as shown in Table 6-3 and Table 6-4. As per assumptions explained in 6.1.1 and the results from this section so far, the following can be stated:

- Installed main engine: 16,080 kW
- Design point main engine: 50% 13,536 kW & 50% 12,348 kW (average: 12,942 kW)
- Main engine output: 84,123,000 kWh per year
- Main engine efficiency: 50%
- HFO (fuel) consumption: 15,142 ton per year
- DeNOx system is applied as NOx emissions are identified as per 6.1.3
- No scrubber is included as low sulphur 0.5% HFO is used

Component	Figures	Δ CAPEX	Notes
*Main engine	400 €/kW	€6,432,000	Engine manufacturer guideline with added margin
DeNOx	40 €/kW	€643,200	Average of source: [62]
Total		€7,075,200	

Table 6-3: Δ CAPEX, Conventional option

*Including PTO – Shaft generator and AC/AC Frequency Converter

Component	Figures	ΔOPEX 1 year	ΔOPEX 25 years	Notes
*Main engine	2.5% CAPEX	€160,800	€4,020,000	Engine manufacturer guideline with added margin
DeNOx	6 €/MWh	€504,738	€12,618,450	Average of source: [62] Running and maintenance cost
Fuel	500 €/ton	€7,571,000	€189,275,000	Estimation: Low sulphur 0.5% HFO
Total		€8,236,538	€205,913,450	

Table 6-4: ΔOPEX, Conventional option

*Including PTO – Shaft generator and AC/AC Frequency Converter.

This results in ΔTCO of €212,988,650 for the conventional option.

6.2 General Comparison

The comparison of the selected ammonia powered option, the ICE, with the conventional option is shown in Table 6-5 and Table 6-6.

Option	*Power density		Harmful emissions	***Load response	
	[kW/ton]	[kW/m3]		Heavy weather	Port
ICE (NH ₃)	+/-38	+/-29	**+/-14 g/kWh NOx 100ppm ammonia slip	V	V
Conventional	+/-35	+/-32	561 g/kWh CO ₂ 1 g/kWh SOx & PM **14 g/kWh NOx	V	V

Table 6-5: Comparison with Conventional option, Part 1

*Power density is a guideline based on simplified measurements of the engine. Other equipment such as support systems and electrical systems are excluded.

**Emissions of main engine, apply SCR to reduce NOx as much as possible.

***Load response:

V: System has sufficient capability to cope with conditions

Option	*Part load	Marine environment	System efficiency	Total cost of ownership (ΔTCO)
ICE (NH ₃)	V	No issues	49.4%	€689,496,925
Conventional	V	No issues	47.3%	€212,988,650

Table 6-6: Comparison with Conventional option, Part 2

*Part load

V: System has sufficient capability to supply minimum power in port conditions

Reviewing the power density, load response, part load, marine environment and system efficiency both the ICE option and the conventional option perform similarly. The conventional option clearly has significantly more harmful emissions (with NOx assumed to be similar). However, the current related costs are significantly lower. To analyse the potential of ammonia further several future scenarios are studied in 6.3 which influence the cost difference.

6.3 Cost Scenario Comparisons

6.3.1 Scenario 1: Basic

Based on what has been provided in 5.2 and 6.1 the first basic comparison, scenario 1, can be made between ICE (NH₃) option with 850 euro per ton ammonia and the conventional option with 500 euro per ton low sulphur 0.5% HFO. As can be seen in Figure 6-2 the conventional option is significantly cheaper.

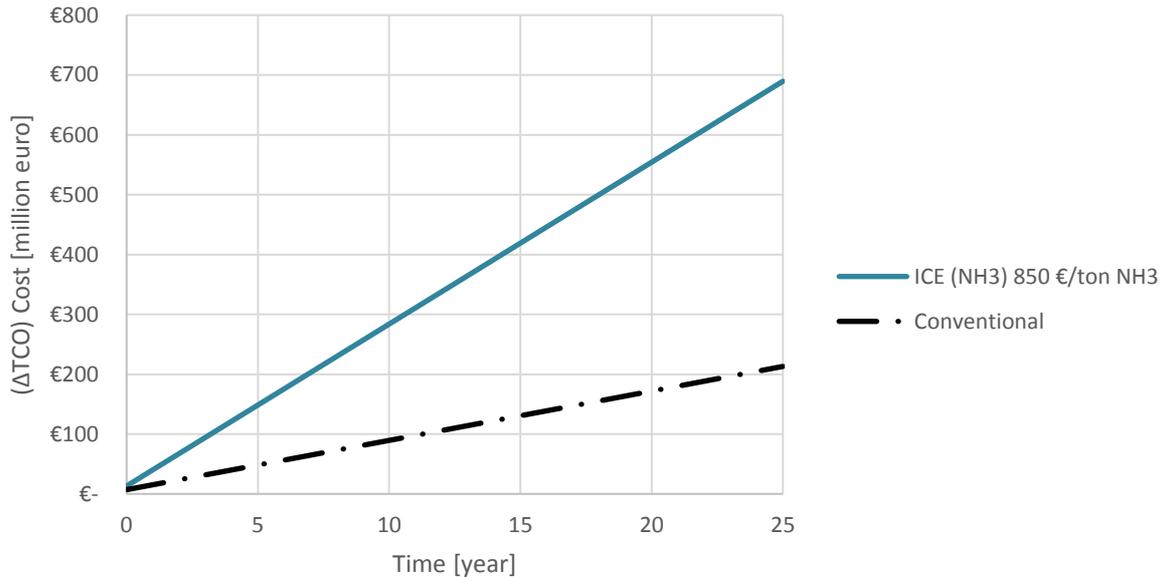


Figure 6-2: Cost scenario 1 comparison ICE (NH₃) vs Conventional

6.3.2 Scenario 2: Emission taxation

Scenario 2 extends the basic scenario with emission taxation resulting in Figure 6-3. As can be seen taxation of 400 euro per ton CO₂ with the conventional option is approximately similar as the ICE (NH₃) option.

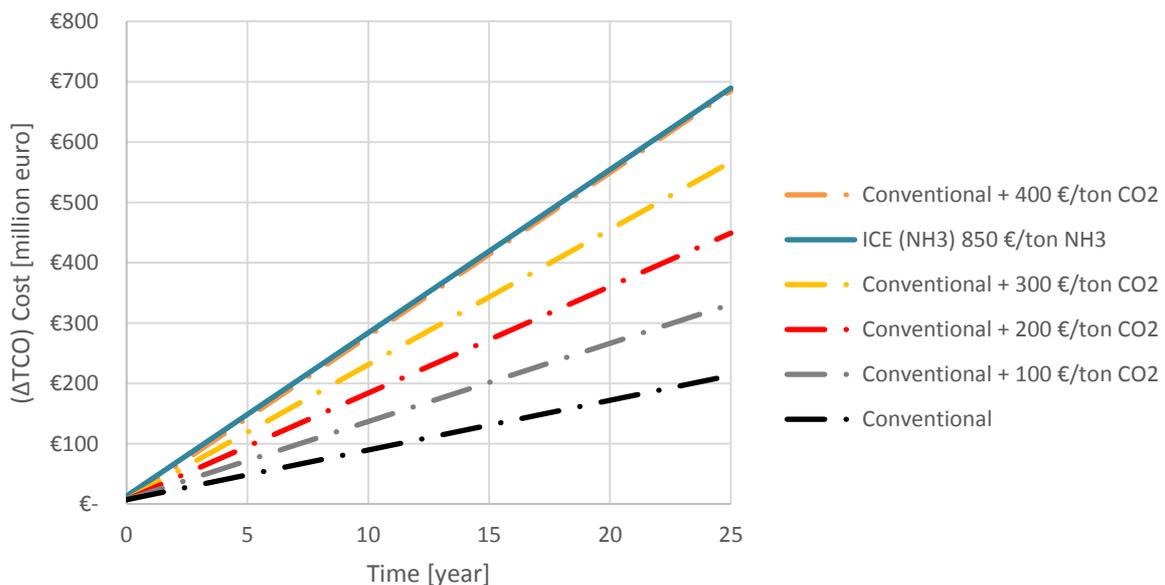


Figure 6-3: Cost scenario 2 comparison ICE (NH₃) vs Conventional

6.3.3 Scenario 3: Low electricity price

In scenario 3 the availability of low-cost electricity is added to the basic scenario enabling 400 euro per ton ammonia. As can be seen in Figure 6-4 the difference between the conventional option and the ICE (NH₃) is significantly reduced. However, there is quite some distance between it and the conventional option.

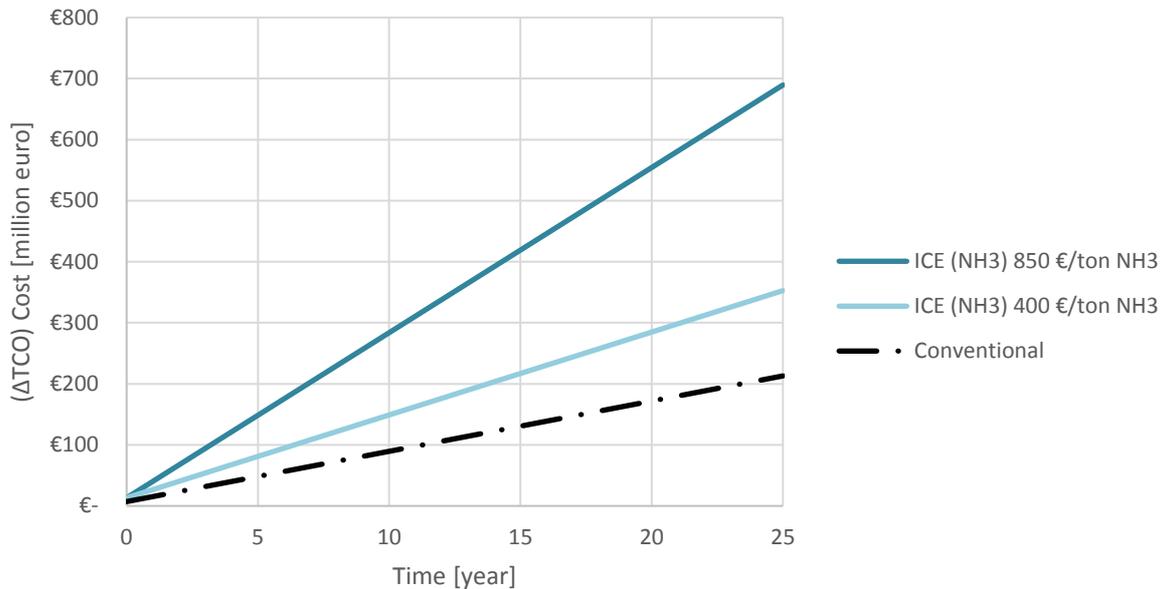


Figure 6-4: Cost scenario 3 comparison ICE (NH₃) vs Conventional

6.3.4 Scenario 4: Combination 2 & 3

Combining the data from scenario 2 and 3 scenario 4 is made. As can be seen in Figure 6-5 the ICE (NH₃) with 400 euro per ton ammonia is on a similar level as the conventional option with 100 euro per ton CO₂.

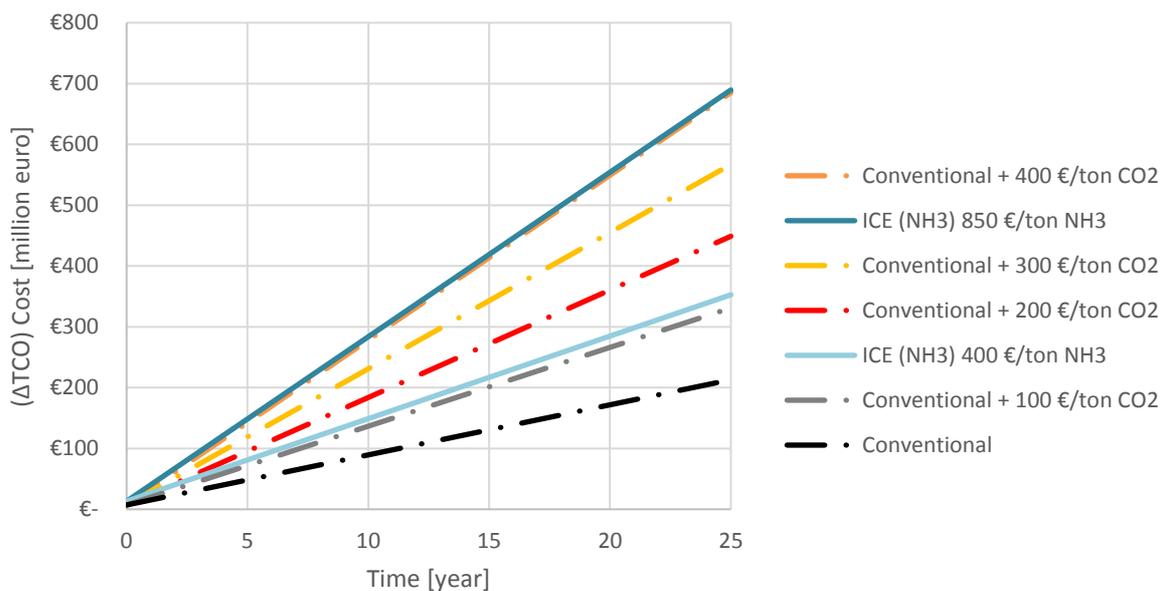


Figure 6-5: Cost scenario 4 comparison ICE (NH₃) vs Conventional

In addition, the same levels can also be reached for the conventional option when low sulphur 0.5% HFO is approximately 811 euro per ton without any CO₂ emission tax. This is based on 6-1. Using this principle relation Figure 6-5 can be converted to Figure 6-6.

$$6-1 \quad HFO - n = HFO - o + (3.114 \times CO_2 - tax)$$

Where:

$HFO - n$	Low sulphur 0.5% HFO cost (new)	€/ton HFO
$HFO - o$	Low sulphur 0.5% HFO cost (old)	€/ton HFO
$CO_2 - tax$	CO ₂ emissions taxation	€/ton CO ₂

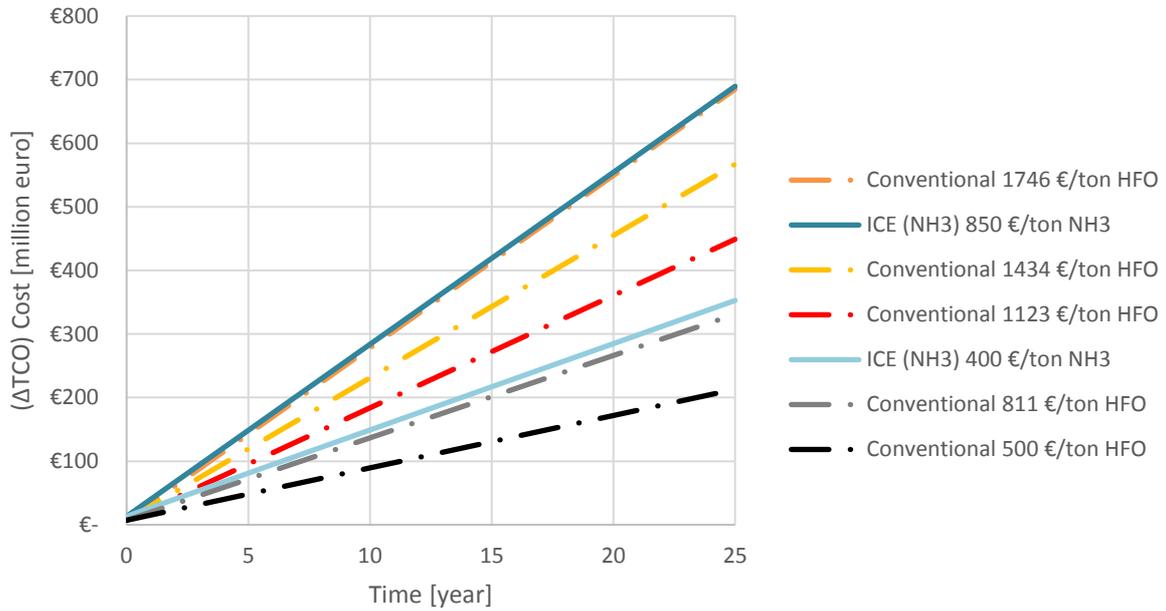


Figure 6-6: Cost scenario 4 comparison ICE (NH₃) vs Conventional, CO₂ tax translated in HFO price

6.3.5 Boil-off influence

Reviewing the other two vessel sizes the influence of using the boil becomes clear. The results of scenario 1, scenario 4 are given in Table 6-7. See Appendix P for the entire cost calculation.

DWT	Difference in Δ TCO: ICE (NH ₃) vs Conventional	
	Scenario 1	*Scenario 4
6,000	250%	17%
18,000	237%	12%
54,000	224%	7%

Table 6-7: Influence boil-off comparison with conventional option

*Based on 400 euro per ton ammonia and 100 euro per ton CO₂

The large vessel, 54,000 ton DWT, has a clear benefit compared to the smallest vessel, 6,000 ton DWT. However, this not fully due to the use of boil-off as the relative impact of less income is bigger for the smaller vessels as shown in Figure 6-7. Nevertheless, the boil off plays its part and will enable large vessels to become economically viable earlier.

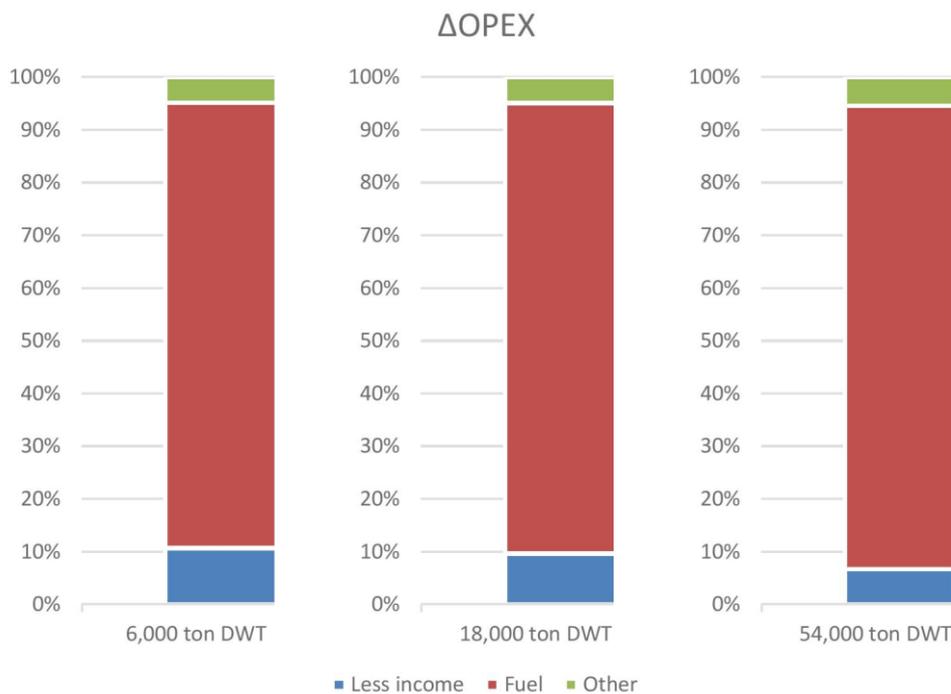


Figure 6-7: Δ OPEX distribution per ship size (Scenario 4: ICE (NH₃) with 400 €/ton NH₃)

6.4 Conclusion

Reviewing the ammonia powered option with the ICE with the conventional option the technical performance is similar on power density, load response, part load performance, coping with marine environment and system efficiency. However, the conventional option has significantly more harmful emissions (with NO_x assumed to be similar).

Studying the basic cost scenario, 850 euro per ton ammonia and 500 euro per ton low sulphur 0.5% HFO, the ammonia powered option is clearly more expensive, about 3.2 times the expenses of the conventional option. Reflecting on future scenarios with 400 euro per ton ammonia, based on low electricity cost, it is in a similar range of 500 euro per ton HFO with 100 euro per ton CO₂ taxation. In addition, this would be similar to 811 euro per ton HFO without CO₂ taxation.

6.5 Recommendations

One of the major advantages is that fuel cells are capable of efficient electrical power generation without any harmful emissions since NO_x emissions are also zero. As fuel cell technology is still undergoing a lot of development it is recommended to maintain an accurate view on the technical and economic performance. Fuel cells might not power vessels today, but with its implementation ongoing in cars, buses, light trains and submarines they could become feasible for vessels for main power generation in the future.

Reviewing 5.6 the SOFC has a lot of potential. However, it does require more development in technical performance such as power density and load response capability. Furthermore, the cost-effectiveness also needs to be improved before it can become economically viable. In addition, besides the SOFC performance, both technical and economical, the global production capacity also needs to be scaled up significantly. The current global production capacity is not considered to be sufficient to realize the power ranges within an acceptable time window.

To cope with the load response challenge of the SOFC a hybrid system could be considered using both SOFC and PEMFC. The thermal energy of the SOFC could be utilized to improve the efficiency of the PEMFC with cracker. Combined with batteries the SOFC can cover the base load and the PEMFC can take the fluctuating loads. This way high efficiency can be combined with adequate load response.

As this study compared fuel cells with an internal combustion engine in a fuel direct configuration the fuel cells had to cope with the losses in the electrical system where the ICE did not have this for most part. Therefore, fuel cells are more attractive at first in vessels which already have fuel electric configurations.

6.6 Outlook

6.6.1 Renewable fuel implementation

The general transition of the implementation of renewable fuel is visualized in a simple graph shown in Figure 6-8. Depending on one's view 2050 can be given a particular position in the timeline.

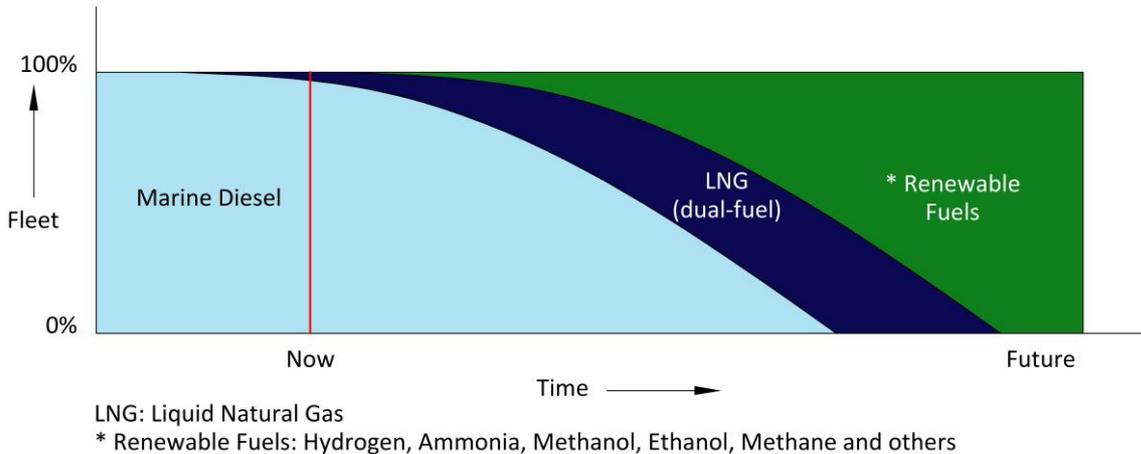


Figure 6-8: Renewable fuel implementation timeline

To implement ammonia as a renewable fuel the possibility of a step wise introduction could be an aid in the speed of adoption. The author considers the following timeline as per Figure 6-9 as possibility.

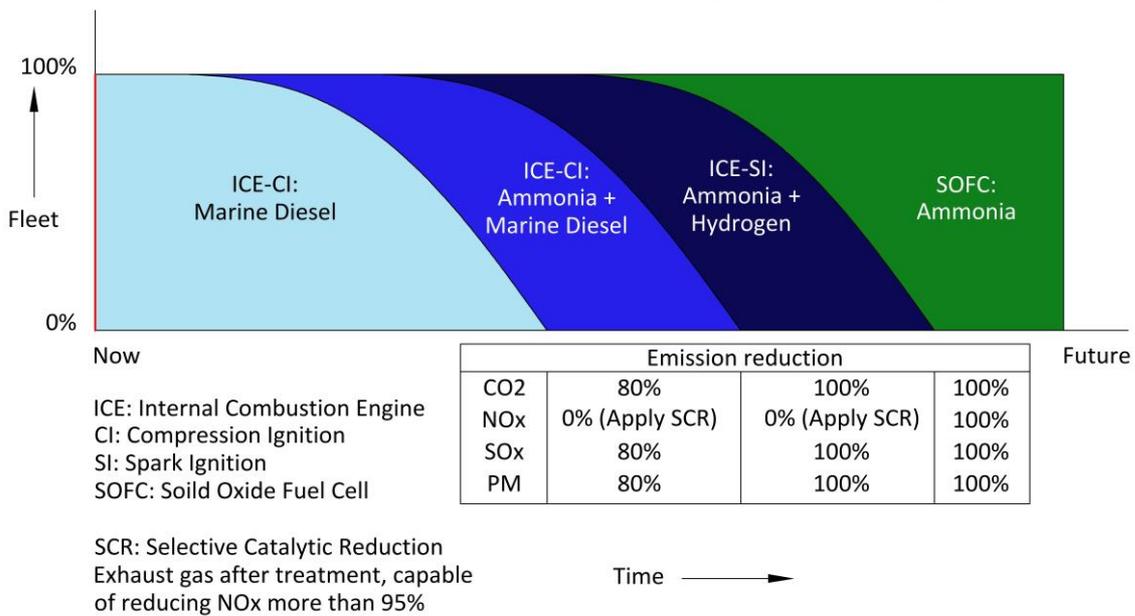


Figure 6-9: Ammonia implementation timeline

In stage 1 ammonia is used with diesel in an ICE, compression ignition, resulting in significant reduction in harmful emissions. This allows the operator to select the amount of ammonia himself offering flexibility to cope with ever changing economic viability to comply with harmful emission reduction regulations in the coming decades. Furthermore, if the ammonia fuel system might fail during operation, as the ammonia fuel system is relatively new, the operator can switch over to 100% diesel. Once the failure is fixed the ammonia can be added again. This way the continues operation is guaranteed. In stage 2 diesel is replaced with hydrogen and instead of compression ignition spark ignition technology is used resulting in a further reduction in harmful emissions reaching zero CO₂, SOx and PM emissions. As final stage, stage 3, the SOFC replace the ICE eliminating NOx emissions as the final harmful emission. Depending on the development speed of the SOFC stage 2 could possibly be skipped.

7 GENERAL AMMONIA SAFETY

In this chapter the hazards of ammonia are addressed and compared with conventional fuels to indicate the area with the main risks. Furthermore, existing general safety measures, rules and regulations and the role of ammonia in the natural nitrogen cycle are studied. This chapter concludes with a review of the discussed topics to indicate the risk levels of ammonia on flammability, toxicity and environmental impact.

7.1 Hazards of Ammonia

To obtain a clear picture on the risks of ammonia hazard statements as safety standard are studied. Hazard statements form part of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). They are intended to form a set of standardized phrases about the hazards of chemical substances and mixtures that can be translated into different languages [78]. In Table 7-1 the hazard statements of ammonia are listed and compared with other fuels.

Hazard statements	Hazard category	Comparison with other fuels				
		Ammonia [79]	CNG [80]	LNG [81]	Diesel [82]	ULSFO [83]
H220 Extremely flammable gas	1A		X	X		
H221 Flammable gas	2	X				
H226 Flammable liquid and vapour	3				X	
H227 Combustible liquid	4					X
H280 Contains gas under pressure; may explode if heated	Compressed gas		X			
	Liquefied gas (b)	X*				
H281 Contains refrigerated gas; may cause cryogenic burn or injury	Refrigerated liquefied gas			X		
H304 May be fatal if swallowed and enters airways	1				X	
H313 May be harmful in contact with skin	5				X	
H314 Causes severe skin burns and eye damage	1B	X				
H315 Causes skin irritation	2				X	
H331 Toxic if inhaled	3	X				
H332 Harmful if inhaled	4				X	X
H350 May cause cancer	1B					X
H351 Suspected of causing cancer	2				X	
H361 Suspected of damaging fertility or the unborn child	2					X
H373 May cause damage to organs through prolonged or repeated exposure	2				X	X
H410 Very toxic to aquatic life with long lasting effects	1	X				X
H411 Toxic to aquatic life with long lasting effects	2				X	

Table 7-1: Hazard statements comparison of ammonia with other fuels

CNG: Compressed Natural Gas

LNG: Liquefied Natural Gas

ULSFO: Ultra Low Sulphur Fuel Oil (0.1%)

H: Hazard statement

2: Physical hazard

3: Health hazard

4: Environmental hazard

Hazard category: a hazard class for which the use of a hazard statement is applicable [78]

*Different from Safety Data Sheet (SDS) [79], corrected accordingly to definition of GHS [78].

7.2 Existing Safety Measures

The main hazard with ammonia is the toxicity. Ammonia is a gas at atmospheric pressure at room temperature which is lighter than air. So, depending on the situation different methods are applied to cope with leakages and unwanted pressure build in ammonia storage systems.

7.2.1 Leakages in enclosed spaces (Air)

To prevent hazardous concentrations of ammonia an enclosed space with a system containing ammonia is continuously vented and monitored by ammonia detectors. Furthermore, in case of an actual leakage additional air ventilation is applied to keep the ammonia concentration as low as possible.

7.2.2 Leakages in open spaces (Water)

In case of leakages in open spaces water spray is often used to dissolve the ammonia in water also known as, ammonia solution or aqueous ammonia. By doing so dispersal of gaseous ammonia is prevented. Depending on the temperature the solubility of ammonia in water varies. At room temperature at atmospheric pressure the solubility of ammonia in water is about 34% by mass. By adding additional water, the concentration of ammonia is lowered further reducing the hazard of its toxicity. In respect ammonia solution for household cleaning purposes is about 5% ammonia by mass.

7.2.3 Overpressure in storage tanks (Fire)

When there are conditions that cause a rise in pressure in the ammonia storage tank ammonia can be released by means of a vent mast maintaining acceptable pressure levels. However, in case this would mean large amounts of gaseous ammonia are released, forming unacceptable concentrations, there is the possibility to burn the ammonia with a flare. In general, the flaring is initiated and maintained by burning natural gas, then the ammonia is added and burned with the natural gas. By doing so the toxicity hazard is eliminated as ammonia is converted mainly into nitrogen and water.

7.3 Rules and Regulations

The invention of the Haber-Bosch process in the first decade of the 20th century enabled the industry to scale up ammonia production and supply the growing global demand [84]. Nowadays, the main consumer of ammonia is the fertilizer industry. The global ammonia production levels are around 180 million ton per year where approximately 10% is transported over sea [85]. Besides fertilizer production ammonia is also used in cooling systems as a refrigerant. Furthermore, ammonia is applied in DeNO_x system, mainly in the form of urea. With decades of industrial experience with ammonia rules and regulation have been formulated for several applications.

7.3.1 Onshore industry

Within the Netherlands there are national guidelines regarding onshore storage and handling of ammonia. These are covered by the Publication series on Dangerous Substances (PGS).

7.3.1.1 PGS 12: Storage and loading of ammonia

The goals of PGS 12 is to cover personnel, environment and fire safety on storage and loading of ammonia. It extends to both pressurized as refrigerated storage regardless of storage volume. It provides qualitative guidelines for ammonia storage and loading on, but not limited to, design and construction of ammonia storage plants, loading stations, operational procedures, inspection and maintenance.

7.3.1.2 PGS 13: Ammonia as refrigerant in cooling installations and heat pumps

Similar to PGS 12, PGS 13 goal is to cover personnel, environment and fire safety yet focussed on cooling system using ammonia. It classifies multiple sizes and types of cooling systems and likewise provides qualitative guidelines for safe design and operation.

7.3.2 Maritime industry

For maritime transport of ammonia several regulations have been developed. Furthermore, applying alternative fuels on ships has also been regulated. The IBC, IGC and IGF code are reviewed in this subsection.

7.3.2.1 IBC Code - International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk, Amended by Resolution MEPC.225(64)

The purpose of the IBC code is to provide an international standard for the safe carriage, in bulk by sea, of dangerous chemicals and noxious liquid substances listed in chapter 17 of the code. The code prescribes the design and construction standards of ships, regardless of tonnage, involved in such carriage and the equipment they shall carry to minimize the risk to the ship, its crew and the environment, having regard to the nature of the products involved.

The IBC code does not cover ammonia it only covers aqueous ammonia (ammonia solution) up to 28%. Therefore, the IBC code is not applicable.

7.3.2.2 2014 IGC Code - International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk

The purpose of the IGC code is to provide an international standard for the safe carriage, by sea in bulk, of liquefied gases and certain other substances that are listed in chapter 19. Through consideration of the products carried, it prescribes the design and construction standards of the ships involved and the equipment they should carry to minimize the risk to the ship, its crew and the environment.

The code covers topics including, but not limited to, ship survival capability and location of cargo tanks, cargo containment, fire safety and use of cargo as a fuel. Highlighting ammonia, it is classed as shown in Table 7-2.

Product name	Ship type	Vapour detection	Gauging	Special requirements
Ammonia, anhydrous	2G/2PG	Toxic	Indirect or closed	14.4, 17.2.1, 17.12

Table 7-2: Summary of minimum requirements, Ammonia, 2014 IGC Code, Chapter 19

The ship type is category 2 meaning that significant preventive measures to preclude escape of cargo are required (where category 1 would be maximum and 3 moderate). The minimum required distance between cargo and the bottom/shell is defined accordingly based on the category. Furthermore, where gas detection is required, regarding the cargo containment system, it must be capable of toxic vapour detection. For ammonia, no flammable vapour detection is required as per summary of requirements of the IGC code regarding the cargo containment system. The IGC Code also has a chapter dedicated regarding the use of cargo as a fuel. However, this is only applicable for methane/LNG.

7.3.2.3 IGF Code - International Code of Safety for Ships Using Gases or Other Low-Flashpoint Fuels

The purpose of the IGF code is to provide an international standard for ships using low-flashpoint fuel, other than ships covered by the IGC code.

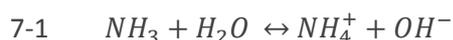
The IGF code is a general foundation for ships using gases or other low flashpoint fuels. The first draft was initiated in 2005 and in 2017 it has been fully developed and adopted for natural gas. These developments enabled ships other than LNG carriers to use LNG as a fuel. The IGF code is still being further developed for other fuels besides natural gas.

7.4 Ammonia in the Nitrogen Cycle

In a natural state ammonia can both be present in the atmosphere and in the ocean. In the pristine marine boundary layer, atmospheric NH₃ concentrations are extremely low [86]. Depending on the concentration in either one of them the flux has a certain direction. For example, high atmospheric NH₃ concentrations can lead to a net flux of NH₃ from the atmosphere to the ocean [87] [88] [89] [86]. However, other studies have also pointed out that even at low atmospheric NH₃ concentrations the coastal North Sea is a sink for atmospheric NH₃ [90] [86].

Gaseous NH₃ in the atmosphere dissolves in rain droplets as ammonium [86]. Moreover, NH₃ can form NH₄⁺ salts (NH₄⁺ aerosols) by rapid gas-to-particle conversion [91] [86]. Thus, NH₃ plays a unique role in the formation of tropospheric aerosols. Because of its basic character it neutralizes acidic sulphuric acid-water aggregates by forming ammonium sulphate aerosols which can act as cloud condensation nuclei [91] [92] [86]. Therefore, NH₃, as a precursor of clouds and other aerosols, is of considerable importance for the Earth's atmosphere's composition, chemistry and climate [86].

Atmospheric NH₃ in the present-day marine boundary layer has a short life time ranging only a few hours to days [93] [94] [86]. NH₃ and NH₄⁺ in the marine boundary layer are mainly removed by dry and wet deposition to the ocean [86]. Other natural sources of ammonia in water can be, but not limited to, fish waste and decomposition of organic matter. When ammonia is dissolved in water it reacts as a base as shown in 7-1 [86].



The equilibrium is influenced by the pH and temperature of the water. The balance between ammonia, NH₃, and ammonium, NH₄⁺, in water is given in Table 7-3 [95] [96]. The pH of seawater varies between approximately 7.9 and 8.25 [97].

pH	mol Ammonia NH ₃	mol Ammonium NH ₄ ⁺	mol NH ₃ /NH ₄ ⁺
7.25	1%	99%	1:100
8.25	9%	91%	1:10
9.25	50%	50%	1:1

Table 7-3: Fraction of chemical species of ammonia present with change in pH (at 25°C)

Where NH₃ is toxic NH₄⁺ is significantly less toxic and also one of the essential nutrients in the oceans [98] [86]. NH₄⁺ is the substrate or final product of major biological transformation processes of the oceanic nitrogen cycle such as bacterial nitrification assimilation by phytoplankton and excretion by zooplankton. As summary, a simplified scheme of NH₃/NH₄⁺ cycling in the marine boundary and ocean surface layers is shown below in Figure 7-1 [86].

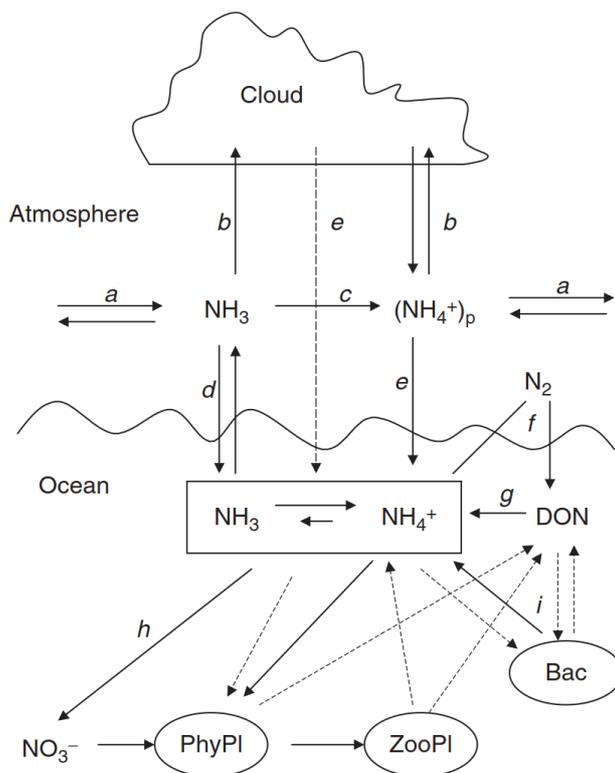


Figure 7-1: Simplified scheme of NH₃/NH₄⁺ cycling in the marine boundary and ocean surface layers. Exchange processes of NH₄⁺ across the ocean/sediment interface are not shown. (NH₄⁺)_p stands for particulate NH₄⁺ (NH₄⁺ aerosol), DON stands for dissolved organic nitrogen, PhyPI and ZooPI stand for Phytoplankton and Zooplankton respectively, and Bac stands for bacteria. Dashed arrows depict uptake/assimilation and release/excretion. Small letters in italics represent physical, chemical, and biological processes: *a*, atmospheric transport processes; *b*, uptake and release in clouds; *c*, gas-to-particle conversion; *d*, gas exchange; *e*, wet and/or dry deposition; *f*, nitrogen fixation; *g*, photochemical decomposition, *h*, nitrification; *i*, decomposition. The scheme is copied from [86].

7.5 Risk Levels

Reviewing the discussed topics hazards of ammonia, existing safety measures, rules and regulations, and ammonia in the nitrogen cycle the risk levels on each category can be summarized.

7.5.1 Flammability

Reviewing 7.1 ammonia has lower flammability risk than natural gas since it is listed in category 2 of flammable gases. This can be explained by several factors, like:

- A narrow flammability limit: 15-28% [10], with a high lower limit compared to other fuels
- A high absolute minimum ignition energy compared to other fuels [10]
- A high auto ignition temperature: 651 °C [10]

Furthermore, toxicity limits, which will be addressed in the next subsection, are far more severe than flammability limits for ammonia. This is also seen in the IGC code since only toxic vapour detection is required. Nevertheless, ammonia is a flammable gas thus ignition sources should be kept away sufficiently in order to prevent fires. In addition, likewise with natural gas ammonia contains gas under pressure; may explode if heated. So, means for pressure relieve should be installed accordingly.

7.5.2 Toxicity

As shown in 7.1 ammonia has two distinct different health hazards compared to conventional fuels. Ammonia causes severe skin burns and eye damage and is toxic if inhaled. Since ammonia is a gas at atmospheric conditions the risk of exposure is very real. Based on Acute Exposure Guideline Levels (AEGL) the limits to ammonia exposure can be identified as shown in Table 7-4.

(ppm)	10 min	30 min	60 min	4 hr	8 hr
AEGL 1	30	30	30	30	30
AEGL 2	220	220	160	110	110
AEGL 3	2,700	1,600	1,100	550	390

Table 7-4: Acute Exposure Guideline Levels (AEGL): Ammonia

AEGL 1: Notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL 2: Irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: Life-threatening health effects or death.

To reduce the likelihood of exposure to high concentrations adequate ventilation should be installed in all areas where ammonia gas could be built up. In case the ejected concentration would be too high with ventilation or a significant leak emerges, the hazard can be contained by means of water spray dissolving the ammonia into water. Both release of ammonia into air and water have an impact on the environment which will be discussed in the next subsection.

7.5.3 Environmental impact

An ammonia spillage in water leads to several things. When liquid ammonia is spilled directly into water approximately 70% will dissolve into the water [99] forming a balance of mostly ammonium and a little ammonia depending on the pH and temperature of the water. The remaining 30% will evaporate as at the moment of spillage locally insufficient water is available to dissolve all the ammonia resulting in a gas cloud.

The dissolved ammonia is a serious threat to aquatic organisms killing most in close proximity as lethal concentrations are easily exceeded. Especially fish are more sensitive to ammonia than plants and other underwater organisms [100]. In the longer term the ocean will require time to recover as the ammonia is converted by bacteria 'Nitrosomonas' to nitrite (NO_2^-) and later by 'Nitrobacter' to nitrate (NO_3^-) which can then be used by plants. As this process consumes parts of the available oxygen in the water the oxygen for other organisms is limited. In addition, the dissolved ammonium, which will mainly be consumed by aquatic organisms such as algae, are also responsible for limiting the amount of available

oxygen. Therefore, the return of aquatic organisms higher in the food chain, like fish, will take a significant amount of time as the lack of oxygen limits the rate of their return. This confirms and to a certain extent explains the environmental hazard of ammonia 'Very toxic to aquatic life with long lasting effects'. Ammonia kills most living organisms in close proximity and its effects demand a serious amount of time to restore the area to its natural state.

An ammonia gas cloud can be caused by the remaining 30% of liquid ammonia spillage in water, as discussed earlier, or by liquid ammonia spillage in open air which evaporates. An ammonia gas cloud will rise up in the atmosphere as ammonia gas is lighter than air. Nevertheless, an ammonia gas cloud is a serious threat to organisms in its surroundings as it could easily expose them to lethal concentrations. As it will take time for all the ammonia to evaporate and steadily go up into the atmosphere it will remain a threat. Once diluted in the air it will find a new balance between the atmosphere and ocean over a certain amount of time restoring to its natural state.

8 GENERAL HYDROGEN SAFETY

Since part of the ammonia is cracked into hydrogen, in the selected configuration with internal combustion engine, part of the ammonia fuel system also contains hydrogen. Therefore, general hydrogen safety is also studied covering the hazards and indicating the risk levels of hydrogen on flammability, toxicity and environmental impact.

8.1 Hazards of Hydrogen

To obtain a clear picture on the risks of hydrogen hazard statements as safety standard are studied. In Table 8-1 the hazard statements of hydrogen are listed and compared with other fuels.

Hazard statements	Hazard category	Hydrogen [101]	CNG [80]	LNG [81]	Diesel [82]	ULSFO [83]
H220 Extremely flammable gas	1A	X	X	X		
H221 Flammable gas	2					
H226 Flammable liquid and vapour	3				X	
H227 Combustible liquid	4					X
H280 Contains gas under pressure; may explode if heated	Compressed gas	X	X			
	Liquefied gas (b)					
H281 Contains refrigerated gas; may cause cryogenic burn or injury	Refrigerated liquefied gas			X		
H304 May be fatal if swallowed and enters airways	1				X	
H313 May be harmful in contact with skin	5				X	
H315 Causes skin irritation	2				X	
H332 Harmful if inhaled	4				X	X
H350 May cause cancer	1B					X
H351 Suspected of causing cancer	2				X	
H361 Suspected of damaging fertility or the unborn child	2					X
H373 May cause damage to organs through prolonged or repeated exposure	2				X	X
H410 Very toxic to aquatic life with long lasting effects	1					X
H411 Toxic to aquatic life with long lasting effects	2				X	

Table 8-1: Hazard statements comparison of hydrogen with other fuels

8.2 Risk levels

8.2.1 Flammability

Likewise, with natural gas hydrogen is an extremely flammable gas. It has a very wide flammability bandwidth, ranging from 4% to 74% [101]. Furthermore, it contains gas under pressure, may explode if heated. So, means for pressure relieve should also be installed accordingly.

8.2.2 Toxicity

Hydrogen is not toxic as can also be seen in Table 8-1 as no health hazards are identified. However, likewise with natural gas hydrogen may displace oxygen and cause rapid suffocation. This would on the other hand already exceed the allowable limits regarding flammability.

8.2.3 Environmental impact

Hydrogen is not a hazard to the environment as none are identified in Table 8-1.

9 RISK ASSESSMENT METHODOLOGY

The objective of the risk assessment is to help eliminate or mitigate any adverse effect to the persons on board, the environment or the ship [102] [103]. Typically, a risk assessment consists of the following steps:

- Identification, where the risk is identified
- Analysis, where the risk is quantified
- Assessment, where the risk is prioritized/ranked
- Mitigation, where the risk is eliminated, reduced or prevented

9.1 Risk Identification

The purpose of identification is to obtain a consistent and structured list of all risks studied in this project. To do so the system under consideration will be divided into nodes to assure an overview can be maintained to check consistency and completeness accordingly.

Risks include external sources like flooding, fire, impact and blackout. Furthermore, internal sources in the sense of equipment failure resulting in limited to zero operability, blockages and leakages are also included. Where external is considered all sources outside the ammonia fuel system and internal the components within the ammonia fuel system.

In addition to these mentioned internal and external risks hidden failures will also be reviewed. A hidden failure could occur in for example a 2 x 100% redundant system where the second system is supposed to take over the first system in case the first system fails. In such an event it could be possible that the second system already failed earlier without being detected and thus is unable to take over. With this addition an important boundary condition of redundancy as mitigation is covered.

9.2 Risk Analysis

A risk analysis can be done with a qualitative or quantitative method. For this project the entire risk assessment is performed by a single person with a limited amount of available time. Furthermore, there is no to little quantitative data available to perform the analysis on the ammonia fuel system. One of the reasons for this lack of data is that this is the first known risk analysis for an ammonia fuel system for a vessel. Therefore, the risk analysis will be done with a qualitative method. Furthermore, everything will be based on a single point of failure principle and common causes. The likelihood of multiple failures is considered very low. Furthermore, insufficient time is available to cope with the gained complexity if multiple points of failures would be studied. Therefore, multiple point of failure scenarios are out of scope of this project. Multiple point of failure scenarios could be reconsidered in a later design stage.

9.3 Risk Assessment

The risk assessment will be addressed in line with the risk analysis method thus primarily based on a qualitative method. A risk matrix will be used to rank each risk along severity and likelihood accordingly. Risk matrices are also used in risk assessments required in accordance with the IGF code [102] [103]. The IGF code is the international code of safety for ships using gases or other low-flashpoint fuels. The risk matrix used in this project adopted the risk matrices, described in the IGF code, combining persons on board, ship assets and environment in one table. As this is the first qualitative risk assessment for an ammonia fuel system on board a vessel a conservative approach is applied. This resulted in an increased area of high/intolerable risks and adjusting the other two areas of medium and low risks accordingly in the risk matrix. The risk matrix that is used for this project is shown in Table 9-1. The severity is rated by a letter ranging from A to E. The likelihood is rated by a

number from 1 to 5. Each risk is rated both by severity and likelihood resulting in a combination of a letter and a number, for example D2. Severity is both rated for people, assets and the environment. In the risk assessment the worst case of either 3 will be taken.

Multiple fatalities	Catastrophic damage	E					
*Single fatality	Major damage	D					
Major injury	Localised damage	C					
Minor injury	Minor damage	B					
Zero injury	Zero damage	A					
People	Assets/ Environment		1	2	3	4	5
Severity ↑		Chance	Remote	Extremely Unlikely	Very Unlikely	Unlikely	Likely
		Chance per year	$<10^{-6}/y$	$\geq 10^{-6}/y$ $<10^{-5}/y$	$\geq 10^{-5}/y$ $<10^{-4}/y$	$\geq 10^{-4}/y$ $<10^{-3}/y$	$\geq 10^{-3}/y$
Likelihood →		Chance in Vessel Lifetime	<1 in 40,000	≥ 1 in 40,000 <1 in 4,000	≥ 1 in 4,000 <1 in 400	≥ 1 in 400 <1 in 40	≥ 1 in 40

Table 9-1: Risk matrix, People, Assets and Environment combined

People

Zero injury: No injuries

Minor injury: One or multiple individuals with short-term health effects

Major injury: One individual with long-term health effects

*Single fatality: One death or multiple individuals with long-term health effects

Multiple fatalities: Multiple deaths

Assets

Zero damage: No damage

Minor damage: An event halting operation for less than 3 days

Localised damage: An event halting operation for more than 3 days but less than a month

Major damage: An event halting operation for more than a month but less than 6 months

Catastrophic damage: An event halting operation for more than a 6 months or loss of ship

Environment

Zero damage: No damage

Minor damage: Limited and reversible damage in immediate vicinity

Localised damage: Significant but reversible damage in immediate vicinity

Major damage: Extensive long-term damage

Catastrophic damage: Extensive very long-term or irreversible damage

Colour code

Red-High risk: Unacceptable risk, additional or alternative mitigation measures must be taken

Yellow-Medium risk: Tolerable risk, additional or alternative mitigation measures to be taken unless judged impractical or when cost would be disproportionate to risk reduction

Green-Low risk: Acceptable risk, to be readdressed in a later design stage

9.4 Risk Mitigation

Based on the results of the risk assessment mitigation measures will be reviewed and taken where deemed necessary. In general engineering judgement will be the main guideline.

9.5 Work Flow Example

With all four steps clarified they can be translated into a work flow. The structure and reasoning of the work flow is described in this section based on the example given below in Table 9-2 and Table 9-3.

Reference	Failure Mode	Cause	Effect	Detection	Original Risk Ranking
1-3-01	Ammonia leakage	Various	Engine room exposed with gaseous ammonia	None	E5

Table 9-2: Part I: Risk assessment work flow methodology example: Identification, Analysis and Assessment

Reference	Mitigation	Overall Assessment	Final Risk Ranking
1-3-01	<ol style="list-style-type: none"> 1. Reduce exposed length ammonia piping length in engine room 2. Apply double-walled vented piping in engine room 3. Add ammonia detectors in engine room and within double-walled vented piping 4. Add main isolation valves 	Chances reduced by exposed length reduction. Impact reduced by application of double-walled piping in engine room. Impact further reduced by adding ammonia detectors and main isolation valves which close when an ammonia leakage occurs. Ammonia piping outside of engine room to be reviewed separately.	C2

Table 9-3: Part II: Risk assessment work flow methodology example: Mitigation

9.5.1 Reference

A code given in the column Reference providing an ID of a particular risk. The numbering is built up as follows: Node number – Subsection number - Risk number. The node number is the number of the corresponding section. The subsection number defines an area as part of the domain covered by the node. The risk number is the risk numbered accordingly of all risks considered for a particular node within a subsection.

9.5.2 Failure Mode

The column Failure Mode provides a description of the failure mode.

9.5.3 Cause

The column Cause provides a description of how the failure mode could occur.

9.5.4 Effect

In the column Effect a description of the effects a failure mode can have.

9.5.5 Detection

In the column Detection a description of the installed means for detection of the effects are provided. In case no detection is installed this column will be left empty. Adding detectors is covered under mitigation.

9.5.6 Original Risk Rating

The column Original Risk Rating gives the score of the assessed risk accordingly based on Table 9-1 based on the effects without mitigation.

9.5.7 Mitigation

Based on the Original Risk Rating the level of required mitigation is identified. In column Mitigation the selected mitigations are described.

9.5.8 Overall Assessment

A short description of the effects of mitigation is provided in column Over Assessment.

9.5.9 Final Risk Rating

The column Final Risk Rating gives the score of the assessed risk accordingly based on Table 9-1 based on the effects with mitigation.

10 AMMONIA AS MARINE FUEL RISK ASSESSMENT

To identify the risks and required mitigations of using ammonia as a marine fuel a risk assessment is performed which will be presented in this chapter. The first section will explain the working principle of the technical basis of the ammonia fuel system. This system will be used for the first risk assessment. The first risk assessment will result in a new ammonia fuel system design which will be reflected upon. After the reflection the new ammonia fuel system will be used for a second risk assessment as an additional check. Combined the process will cover two iterations of risk assessment and design. This chapter will finish with a conclusion and recommendations covering the identified risks, required mitigations and design consequences.

10.1 Technical Basis System Diagram

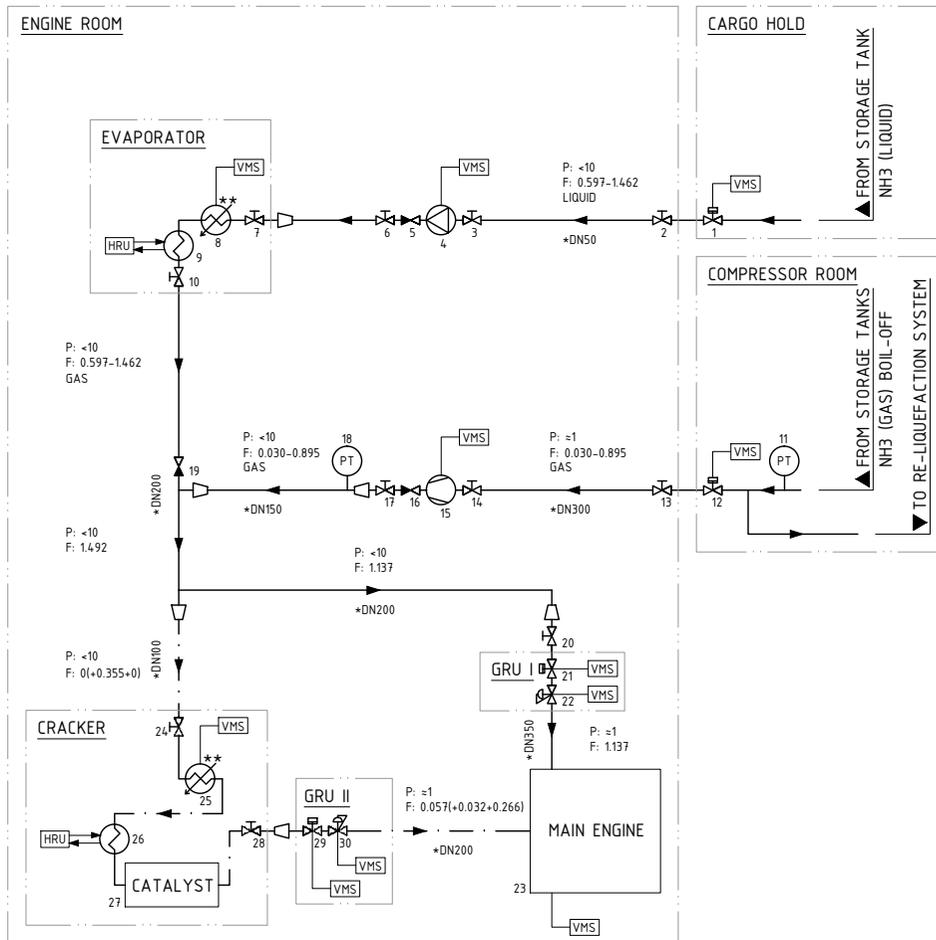
To identify all risks and required safety measures with the risk assessment the ammonia fuel system diagram used will only contain the technical required components to function in normal conditions. Thus, the ammonia fuel system diagram used will have zero safety measures at the start of the risk assessment and serves as a technical basis. With this method all required measures to assure the safety can be clearly identified. The ammonia fuel system diagram consists of four parts namely, main liquid ammonia supply, main gaseous ammonia supply, ammonia engine supply and hydrogen engine supply. The working principle of the ammonia fuel system is explained in this section. See the next page for the technical basis of the ammonia fuel system diagram. It is also provided in Appendix Q combined with a version where the nodes are marked.

10.1.1 General design NH3 fuel system diagram

The entire system is setup for a 54,000 ton DWT ammonia carrier with an ICE using an ammonia hydrogen mixture as per Table 5-5. The system is capable of fuel supply to accommodate 100% power output. The following corresponding data as per Table 10-1 is used to size the system.

Ship	
DWT [ton]	54,000
Main engine [kW]	14,310
Main ammonia supply	
Gaseous ammonia supply (boil-off) [kg/s]	0.030-0.895
Liquid ammonia supply (additional) [kg/s]	0.597-1.462
Fuel	
Ammonia flow [kg/s]	1.169
Hydrogen flow [kg/s]	0.057
Supply	
Direct ammonia flow [kg/s]	1.137
Pre-cracked	
Indirect ammonia flow [kg/s]	0.355
Cracked	
Hydrogen flow [kg/s]	0.057
Ammonia flow (non-cracked) [kg/s]	0.032
Nitrogen flow [kg/s]	0.266

Table 10-1: Design parameters NH3 fuel system diagram



SYMBOLS

	HAND OPERATED VALVE		REMOTE OPERATED VALVE
	NON RETURN VALVE		PRESSURE REGULATING VALVE
	REDUCER		PRESSURE TRANSMITTER
	COMPRESSOR		CENTRIFUGAL PUMP
	HEAT EXCHANGER		HEATER

LEGEND

— NH3 FUEL
 - - - H2(+NH3+N2) FUEL

NOTES

PIPE INDICATION:
 P: PRESSURE bar
 F: FLOW kg/s
 STATE OF MATTER (GAS, UNLESS NOTED OTHERWISE)

HRU: EXHAUST GAS HEAT RECOVERY UNIT
 GRU: GAS REGULATING UNIT
 VMS: VESSEL MANAGEMENT SYSTEM (POWER SUPPLY AND CONTROL)

*) PROVISIONAL DIMENSIONS
 **) START-UP POWER ONLY

INERT GAS SYSTEM TO EMPTY FUEL LINES FOR MAINTENANCE TO BE ADDED

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10.1.2 Main liquid ammonia supply

Depending on the demand of the main engine and the amount of boil-off additional fuel can be obtained from the ammonia from the storage tanks. Based on the pressure transmitter the pump can provide additional flow increasing also the pressure towards the main gaseous ammonia supply. After the pump either the heater (during start up) or the heat exchanger (during continuous operation) heats up the ammonia to turn the liquid ammonia into gaseous ammonia. Once the ammonia has evaporated it can be supplied accordingly to the main gaseous ammonia supply. When shut down the remote operated valve can be closed to stop the flow.

10.1.3 Main gaseous ammonia supply

Depending on the demand of the main engine and the amount of boil-off a certain amount of boil-off can be used for fuel. The boil-off from the cargo tanks is collected in the compressor room and from there redirected towards the engine room. In the engine room the compressor uses the two pressure transmitters to determine the flow it can provide. In case not all the boil-off is consumed the pressure in the supply line to the compressor will increase which will activate the re-liquefaction system to prevent overpressure. The compressor increases the pressure in the supply line from the compressor so it can be added to the rest of the gaseous ammonia supply and distributed accordingly. When shut down the remote operated valve can be closed to stop the flow.

10.1.4 Ammonia engine supply

From the main gaseous ammonia supply the ammonia engine supply is fed. In the ammonia engine supply the pressure is regulated by a pressure regulating valve. The flow is regulated by the main engine. When shut down the remote operated valve can be closed to stop the flow.

10.1.5 Hydrogen engine supply

From the main gaseous ammonia supply the hydrogen engine supply is fed. In the hydrogen engine supply the ammonia is first cracked into hydrogen by heating up the ammonia with either the heater (during start up) or heat exchanger (during continuous operation) and sending the heated ammonia through a catalyst. Once cracked in the catalyst the hydrogen is sent to the engine where the main engine regulates the flow and the pressure regulating valve regulates the pressure. When shut down the remote operated valve can be closed to stop the flow.

10.2 Risk Assessment 1

The method for risk assessment has been defined in chapter 9 and the general required knowledge on ammonia and hydrogen safety has been addressed in chapter 7 and 8 respectively. Combined the risks of the technical basis of the ammonia fuel system diagram can be assessed.

10.2.1 Scope and assumptions

The scope and assumptions of the risk assessment of the ammonia fuel system diagram are defined as following:

- All components are considered to have zero leakage in normal operational conditions
- The cargo system (ammonia storage) is covered within existing regulations for an ammonia carrier and is therefore out of scope
- Inert gas system to empty fuel lines for maintenance is out of scope and to be added in similar fashion as applied in the cargo system
- Main engine assumed to be inherently safe considering fuel injection
- Failure modes of exhaust gas heat recovery unit out of scope
- Access/connecting spaces to spaces covered in the assessment are out of scope
- Ammonia (and hydrogen) that enters the fuel system is treated as fuel and no longer as cargo

10.2.2 Main risks: Identification, analysis and assessment

The basis of the failure modes as defined in 9.1 are used to define all failure modes for each type of equipment and space. See Appendix R for all included failure modes. Using these failure modes, a walk-through of the entire system resulted in a list of 61 risks. See Appendix S for the entire list of risk assessment 1. Summarizing the risks, it covered:

- Space (and environment) exposure/contaminated with liquid and/or gaseous ammonia
- Space (and environment) exposure with gaseous ammonia and hydrogen
- Increase in temperature and pressure within system
- Loss of propulsion and PTO power
- Shut down of all systems
- Too high pressure of fuel supply
- Unable to supply fuel
- Unwanted continuation of flow
- Counter flow
- Unable to use boil-off as fuel

The result of analysing and assessing these risk effects is given in Table 10-2. As shown, there are multiple unacceptable risks which require mitigation. Furthermore, several tolerable risks have been identified which are to be reviewed if mitigation is sufficiently cost-effective. Mitigation of risks will be discussed in the next subsection.

E	2	4	9	10	
D		3	4	9	
C				1	
B			4	5	
A			2	8	
	1	2	3	4	5

Table 10-2: Original risk rating results risk assessment 1

10.2.3 Main risks: Mitigation

Following the identification, analysis and assessment of the risks the mitigations are applied accordingly. The following mitigations have been applied to create a safe design of the ammonia fuel system diagram:

- Add redundancy in supply line (from other source located in different space)
- Add space ventilation
- Add (space) ammonia (and hydrogen) detection (with double redundancy)
- Add space fire detection and fire fighting system
- All space systems, transmitters and detectors connected with vessel management system
- Alert capabilities of space systems in case of failure to be included
- Add flow detection
- Add pressure transmitter (with double redundancy)
- Add temperature transmitter (with double redundancy)
- Add pressure relieve system
- Add remote operated isolation valve
- Add fail close on main supply valve
- Route piping with sufficient distance from shell, for example at least B/5 from side
- Locate piping in separate unmanned space as much as possible
- Apply double-walled piping in engine room and add pressure transmitter (with double redundancy)

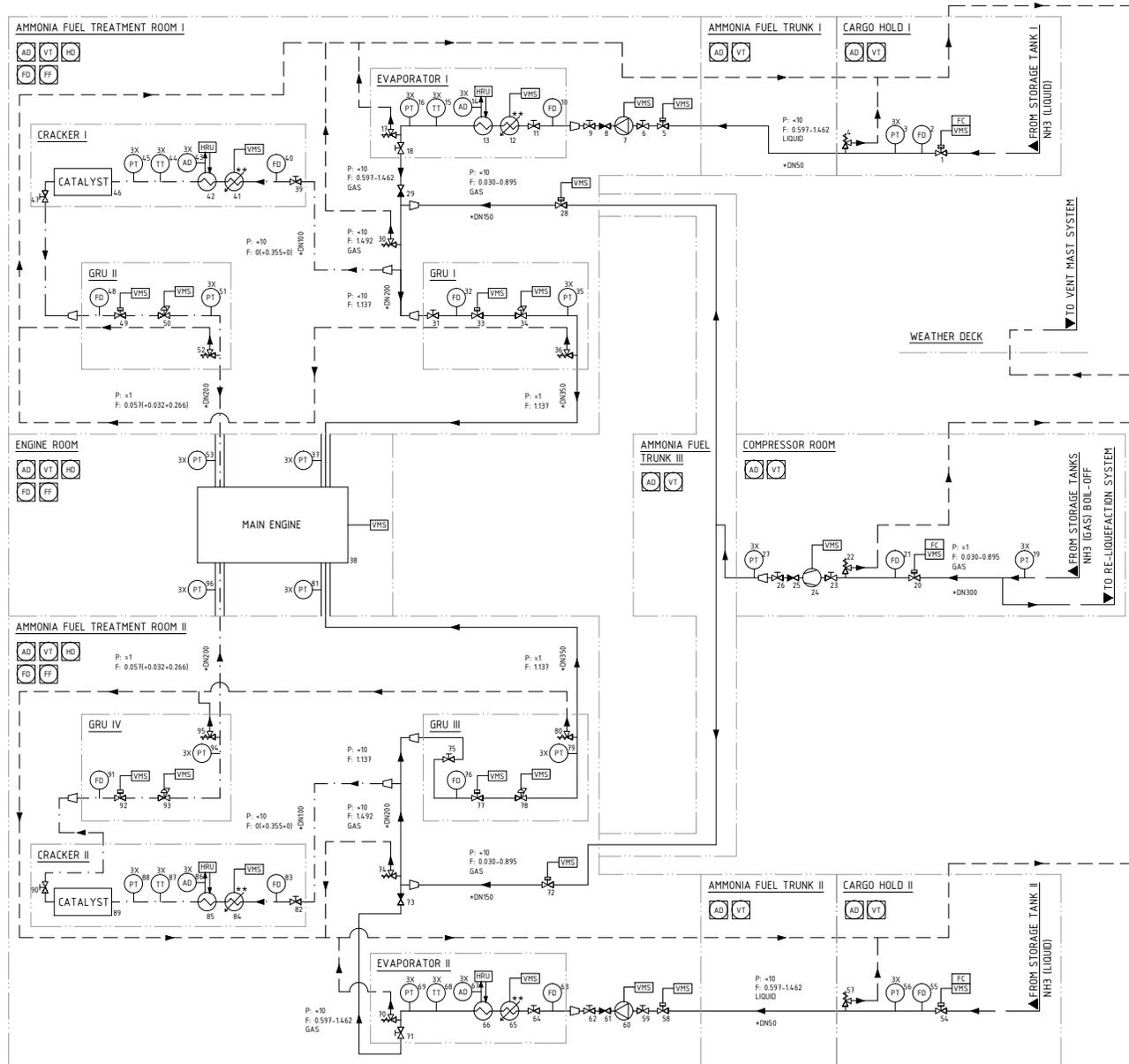
See Appendix S for the entire list of risk assessment 1. Applying these mitigations brings the risks as shown in Table 10-2 to a lower tolerable and acceptable level as given in Table 10-3. See the next page for the new design of the ammonia fuel system diagram (2 x 100%). It is also provided in Appendix T combined with a version where the nodes are marked. This new ammonia fuel system diagram (2 x 100%) will be reflected upon in the next subsection.

E		1			
D	9	1			
C		12		2	
B				2	
A		3	10	21	
	1	2	3	4	5

Table 10-3: Final risk rating results risk assessment 1

With adding the mentioned systems in this sub-subsection special attention is to be given to:

- Ventilation intakes to be located outside hazardous areas
- Hazardous areas of ventilation exhausts to be determined
- Hazardous areas and measures to monitor flow/activity of vent mast to be reviewed
- Additional measures for mitigation of ammonia ventilation either by water spray or flaring to be reviewed.



SYMBOLS

	HAND OPERATED VALVE		REMOTE OPERATED VALVE
	NON RETURN VALVE		PRESSURE REGULATING VALVE
	REDUCER		PRESSURE RELIEVE VALVE
	COMPRESSOR		PUMP
	HEAT EXCHANGER		HEATER
	FLOW DETECTOR		PRESSURE TRANSMITTER
	AMMONIA DETECTOR		TEMPERATURE TRANSMITTER
	SPACE: AMMONIA DETECTION		SPACE: HYDROGEN DETECTION
	SPACE: FIRE DETECTION		SPACE: VENTILATION
	SPACE: FIRE FIGHTING SYSTEM		

LEGEND

	NH3 FUEL
	H2/NH3-N2 FUEL
	AIR/GAS VENT
	NH3 FUEL DOUBLE WALLED
	H2/NH3-N2 FUEL DOUBLE WALLED

NOTES

PIPE INDICATION:
P: PRESSURE bar
F: FLOW kg/s
STATE OF MATTER (GAS, UNLESS NOTED OTHERWISE)

HRU: EXHAUST GAS HEAT RECOVERY UNIT
GRU: GAS REGULATING UNIT
VMS: VESSEL MANAGEMENT SYSTEM (POWER SUPPLY AND CONTROL)
FC: FAIL CLOSE, CLOSSES VALVE IN CASE OF BLACK OUT

+) PROVISIONAL DIMENSIONS
++) START-UP POWER ONLY

1) SYSTEM DESIGN BASED ON ZERO LEAKAGE IN NORMAL OPERATIONAL CONDITIONS, FURTHER ANALYSIS REQUIRED TO CONTINUE DEVELOPMENT OF SYSTEM, FOR EXAMPLE BY MEANS OF QUANTITATIVE ANALYSIS

2) ALL SPACE SYSTEMS, TRANSMITTERS AND DETECTORS CONNECTED WITH VMS

3) REDUNDANCY OF SPACE SYSTEMS TO BE REVIEWED AND LOCAL CAPABILITIES OF SPACE SYSTEMS IN CASE OF FAILURE TO BE INCLUDED

4) INERT GAS SYSTEM TO EMPTY FUEL LINES FOR MAINTENANCE TO BE ADDED

5) ALL FUEL PIPING TO BE ROUTED B/S FROM OUTER SHELL

6) VENTILATION INTAKES TO BE LOCATED OUTSIDE HAZARDOUS AREAS

7) HAZARDOUS AREAS OF VENTILATION EXHAUSTS TO BE DETERMINED

8) HAZARDOUS AREA AND MEASURES TO MONITOR FLOW/ACTIVITY OF VENT MAST TO BE REVIEWED

9) ADDITIONAL MEASURES FOR MITIGATION OF AMMONIA VENTILATION EITHER BY WATER SPRAY OR FLARING TO BE REVIEWED

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(2X 100%)

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CLASS NO.: -

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REVISIONS: -

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10.3 Reflection on Result of Risk Assessment 1

Reflecting on the new ammonia fuel system diagram multiple components have been added to obtain sufficient risk mitigation while maintaining the functionality. The redundancy makes the system bigger and more expensive. As a first setup following the selected mitigations this resulted in 2 x a 100% (maximum power) fuel supply system. The original demand was sufficient fuel supply to the engine meaning adequate ship speed and manoeuvrability can be maintained. 2 x a 50% fuel supply system would in that sense be sufficient as 50% power results in maintaining roughly 80% of the maximum ship speed.

Reducing the redundancy further to a single supply line with only the most critical components redundant would lack the capability to shut-off a supply line completely in case of a leakage. If both supply lines would be in the same space additional measurements would be required to identify the leakage accordingly. In case of a leakage with supply lines in separate spaces it is automatically clear in which line the leakage is located. Furthermore, locating the supply lines in separate spaces remains vital as repairs should only be made in a space shut-off from ammonia supply and sufficiently ventilated. If the supply lines would be in the same space repairs would not be able to be performed during operation. This could possibly limit the operational flexibility and effective use of the vessel.

Based on the reasoning discussed in the previous paragraphs the reflection of the assessment is concluded as following: to keep the impact and likelihood of ammonia exposure towards humans and the environment at an acceptable level it is necessary to have each supply line in a separate space. Reviewing redundancy, a system of 2 x 50% is considered to be the best solution.

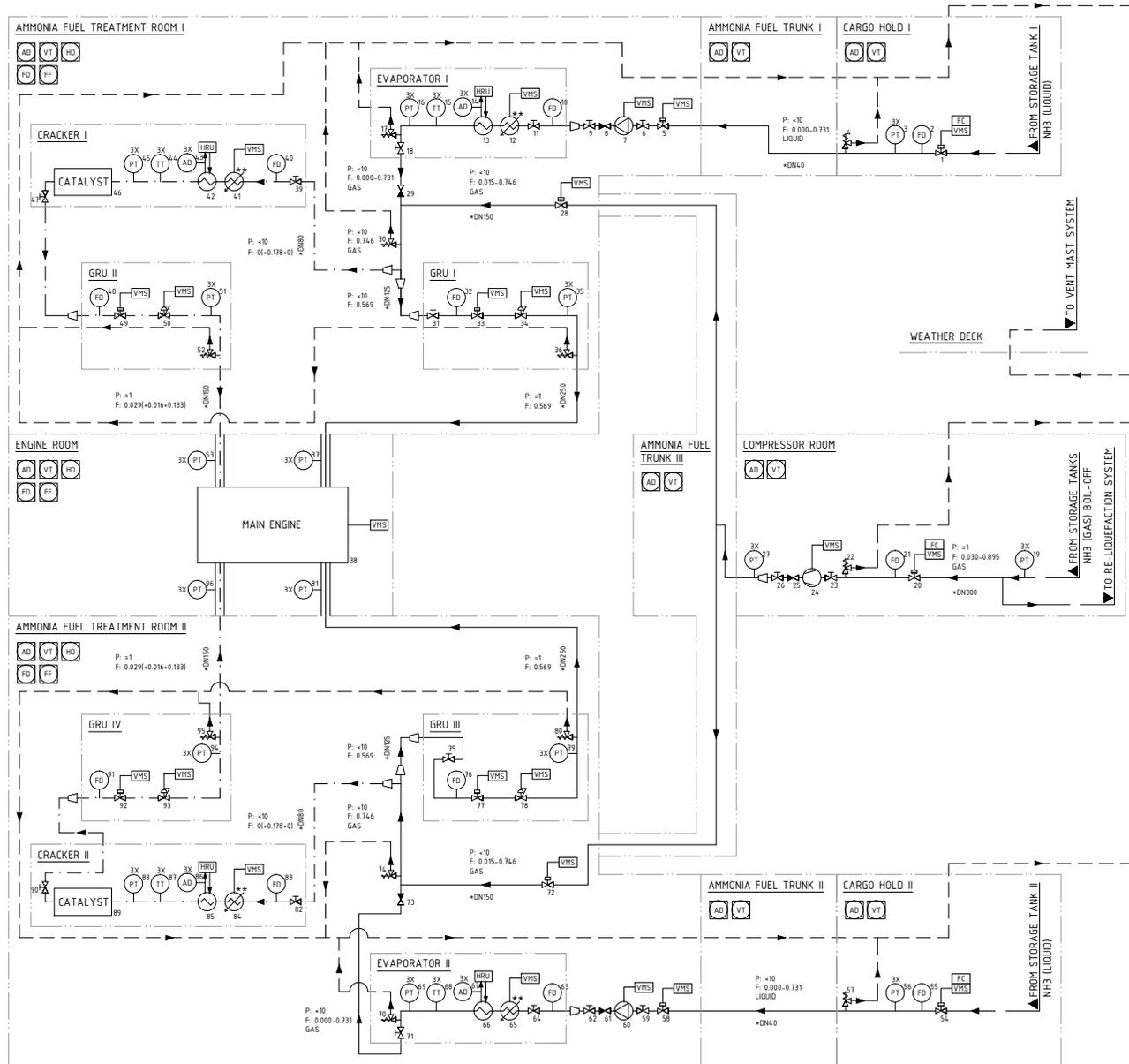
10.4 Risk Assessment 2

To check the impact of the selected mitigations another risk assessment will be done on the new system design. In the previous section it was concluded that 2 x 50% fuel supply system was sufficient with the same distribution in separate spaces as shown in 2 x 100% fuel supply system. See the next page for the new design of the ammonia fuel system diagram (2 x 50%). It is also provided in Appendix U combined with a version where the nodes are marked.

Assessing the system again additional failure modes were identified as new components were added to the system. See Appendix V for all included failure modes. Using all identified failure modes, a walk-through of the entire system resulted in a list of 87 risks. See Appendix W for the entire list of risk assessment 2. Summarizing the risk assessment, it covered:

- Shutting off active fuel supply, continuous ventilation of spaces with fuel supply lines and switching to the second fuel supply line
- Using redundancy of detectors and transmitters to verify measurements
- Releasing a limited amount of ammonia (and hydrogen) by means of a pressure relieve valve to the vent mast
- Cutting air supply to space in case of fire
- Activating fire fighting system in engine room or ammonia fuel treatment room
- Closing a valve to stop limited counter flow

This check concluded that no new unacceptable risks were identified. The results are given in Table 10-4. Furthermore, considering the redundancy applied in the system with 2x 50% is not considered to be sensitive to hidden failures. This is simply due to the fact both systems are both often in operation in normal conditions. For systems with 2x 100% adequate checks and procedures are required to prevent hidden failures.



SYMBOLS

	HAND OPERATED VALVE		REMOTE OPERATED VALVE
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	REDUCER		PRESSURE RELIEVE VALVE
	COMPRESSOR		PUMP
	HEAT EXCHANGER		HEATER
	FLOW DETECTOR		PRESSURE TRANSMITTER
	AMMONIA DETECTOR		TEMPERATURE TRANSMITTER
	SPACE AMMONIA DETECTION		SPACE HYDROGEN DETECTION
	SPACE FIRE DETECTION		SPACE VENTILATION
	SPACE FIRE FIGHTING SYSTEM		

LEGEND

	NH3 FUEL
	H2/NH3-N2 FUEL
	AIR/GAS VENT
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4) INERT GAS SYSTEM TO EMPTY FUEL LINES FOR MAINTENANCE TO BE ADDED

5) ALL FUEL PIPING TO BE ROUTED B/S FROM OUTER SHELL

6) VENTILATION INTAKES TO BE LOCATED OUTSIDE HAZARDOUS AREAS

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TITLE: DIAGRAM NH3 FUEL SYSTEM (2X 50%)

PROJECTION: DIM. UNIT: mm
REVISION: REV. 1 SHEET: 1-1 SCALE: N.A. FORMAT: A1

E		1			
D	11	1			
C		16		2	
B		6		2	
A		3	12	33	
	1	2	3	4	5

Table 10-4: Risk rating results risk assessment 2

10.5 Conclusion

10.5.1 Identified risks

Reflecting on the risk assessment the main specific risks of using ammonia as a marine fuel are ammonia exposure to humans and the environment. In addition, in the fuel supply system considered, the flammability risks of hydrogen, obtained from cracked ammonia, is present. Next to these unique risks the ammonia fuel system has similar risks like other fuel systems covering, unable to supply fuel, main engine failure, too high pressure of fuel supply, increase in temperature and pressure in system, unwanted continuation of flow and counter flow. Considering the vessel type, the inability to use boil-off as fuel is also an effect of the risks considered in the assessment.

10.5.2 Mitigations

To safely handle ammonia (and hydrogen) as a fuel, spaces containing fuel lines should be equipped with ammonia (and hydrogen) detection combined with ventilation. Furthermore, in case of leakages remote operated shut-off valves should be installed to isolate the leakage and limit its impact. In line with this mitigation, redundancy in the fuel supply line should be arranged to ensure sufficient fuel supply for continuous operation in case part of the fuel supply is shut-off. In addition, in case of a blackout the main remote operated isolation valves should be installed with a fail close so when there is a loss of power the valves close automatically. As ammonia exposure to humans and the environment should be limited as much as possible, fuel lines should be routed with a sufficient distance from the shell, for example B/5 from the side. Where possible, fuel lines should be located in separate unmanned spaces. Where impossible, for example in the engine room, double-walled piping with pressure transmitters should be applied.

The ammonia fuel treatment room and similar to other fuel system, the engine room, should be equipped with fire detection and a fire fighting system. Furthermore, to monitor the conditions of the fuel, pressure transmitters, temperature transmitters and flow detectors should be added. In addition, to cope with overpressure a pressure relieve system should be installed.

10.5.3 Design consequences and considerations

The main ship design consequences of the mitigations are on the arrangement due to the required separate spaces for the redundant fuel supply lines covering fuel trunks and fuel treatment rooms. Furthermore, the ventilation of the spaces containing fuel supply lines also require space for the intake and exhaust of air. The requirement of routing with sufficient distance from the side also impacts the effective use of available space of the vessel. All these factors increase the cost, especially the redundancy requirement. Therefore, implementation of 2 x 50% system capacity instead of 2 x 100% is considered to be important to limit these additional costs.

10.6 Recommendations

The developed ammonia fuel system is based on the assumption that there is zero leakage in normal operational conditions. In practice this is not completely valid. For example, when the ammonia fuel system is shut down and the valves are closed, small amounts of gas could leak through a valve. This could cause a slow pressure build-up of ammonia in the fuel supply line towards the engine. To prevent this a block and bleed system after an isolation valve can be applied. Once the system is shut down the bleed valve, connected to the vent system, opens and the block valve closes. The bleed valve allows the minor amount of gaseous ammonia to be vented where the block valves prevents it from going further into the system. Multiple of these examples can be considered. Therefore, further analysis is considered to be required without the zero leakage assumption to continue the development. This should be further investigated and could be done with for example a quantitative safety analysis.

Hazardous areas of ventilation exhausts of spaces containing ammonia fuel lines should be determined by means of additional investigation. In addition, the hazardous area of the vent mast should be reviewed with the addition of the pressure relieve system of the ammonia fuel system. Furthermore, measures to monitor flow/activity of the vent mast including mitigation of ammonia ventilation either by water spray or flaring should be reviewed.

As the main engine is a gas engine fuelled by a mixture of ammonia and hydrogen the reliability of the engine is uncertain at the moment. A main engine failure could have severe consequences as shown in the risk assessment where it is rated E2, a tolerable risk. To reduce this risk cost-effectively a more accurate view on the main engine reliability is required. If the reliability would be considered insufficient, redundancy in the power generation would be needed, requiring two main engines to be installed. This should be further investigated.

As the redundancy requirement in the ammonia fuel system increase cost, further investigation in ammonia diesel combustion is recommended. The application of diesel as pilot fuel would remove the requirement of redundancy in ammonia fuel supply making the system less expensive. In case ammonia cannot be supplied to the engine it can always fall back on full diesel combustion ensuring continuous operation. This way most of the emission reduction potential can be realised yet limiting additional cost while keeping the same amount of operational reliability.

11 CONCLUSION AND RECOMMENDATIONS

11.1 Conclusion

The main research question of this project is: How can ammonia be applied safely and effectively as a marine fuel? To answer the main research question, it is divided into sub questions which are addressed separately below.

11.1.1 What is the potential of ammonia as a fuel in a sustainable future with respect to storage and production?

When comparing ammonia to other renewable fuel options ammonia is considered a balanced solution. Ammonia has a significant higher volumetric energy and has far more practical storage conditions, considering pressure and temperature compared to liquid hydrogen. Furthermore, ammonia requires clearly less energy for renewable synthetic production than carbon carriers. These are the main reasons to further investigate the potential of ammonia as a marine fuel.

11.1.2 What is the technical feasibility of ammonia power generation onshore?

Several options for ammonia power generation have been considered namely: steam turbine, gas turbine, internal combustion engine (both CI and SI) and fuel cells (both PEMFC, AFC and SOFC). Reviewing the physical properties of ammonia and the experiments conducted in the past it is concluded that all of the options considered are technically feasible onshore.

11.1.3 What is the technical feasibility of ammonia power generation for marine applications?

11.1.3.1 Steam turbine and gas turbine

Reflecting on the requirements for marine applications, especially considering the ship type used, an ammonia carrier, efficiency is an important factor. Therefore, both the steam turbine and the gas turbine are not further investigated as feasible option.

11.1.3.2 Internal combustion engine

After comparing application of ammonia and ammonia hydrogen mixtures in internal combustion engines it is clear that ammonia hydrogen mixtures as fuel are preferable if not absolutely necessary. Performance aspects like high compression ratio for CI and low flame speed, low flame stability, limits in operation to cope with ammonia slip (lower combustion efficiency) and NO_x emissions for both CI and SI make pure ammonia less suitable than ammonia hydrogen mixtures for marine applications. Therefore, only ammonia hydrogen mixtures in internal combustion engines are considered technically feasible and further investigated in this project. (Although SI offers more flexibility in design and operation of the engine no specific ignition type, either (HC)CI or SI, is specified as preferable option as both are considered feasible. Whether the additional benefits of SI are of use is for an engine manufacturer to investigate further.)

11.1.3.3 Fuel cells

The considered fuel cells are capable of power generation at high efficiencies using ammonia as primary fuel source. Even though one or more of the considered fuel cell types currently have a low power density and cost significantly more than an internal combustion, future development could improve this. Therefore, all three fuel cell types are further investigated in this project.

11.1.4 What is the performance of ammonia power generation for marine applications?

Reviewing all remaining options (ICE, PEMFC, AFC and SOFC) the SOFC is clearly the most efficient with a system efficiency of 53.9%. However, the SOFC does have practical challenges as the power density and load response capability are not at an acceptable level yet. Furthermore, despite the higher

efficiency of the SOFC the total cost of ownership (Δ TCO) is still higher than the ICE based on these guidelines and estimations. The (two-stroke, low speed) internal combustion engine is second in efficiency with a system efficiency of 49.4% and therefore more efficient than the PEMFC and the AFC with a system efficiency of 44.5% and 44.8% respectively. Furthermore, the ICE is less expensive, more robust and has acceptable power density and load response capability. In the future further development of fuel cell technology might change the outcome of this evaluation. Based on the comparison the ICE is currently selected as best option for this project.

11.1.5 How does conventional power generation compare with ammonia power generation for marine applications?

Comparing the ammonia ICE option with the conventional fossil fuelled ICE option the technical performance is similar on power density, load response, part load performance, coping with marine environment and system efficiency. However, the conventional option has significantly more harmful emissions (with NO_x assumed to be similar). Studying the cost based on equal range the ammonia powered option is clearly more expensive, about 3.2 times the expenses of the conventional option. This follows from a basic cost scenario of 850 euro per ton ammonia and 500 euro per ton low sulphur 0.5% HFO. Looking into future scenarios the ammonia powered option can be in similar cost range as the conventional option. This is the case when using 400 euro per ton ammonia, based on low electricity cost, combined with either a 500 euro per ton HFO with 100 euro per ton CO₂ taxation or 811 euro per ton HFO without CO₂ taxation.

11.1.6 What are the general properties of ammonia in consideration of risk & safety, and how to cope with them?

11.1.6.1 Flammability

Ammonia is a flammable gas. However, ammonia has a relative low flammability risk. This can be explained by several factors like the narrow flammability limits (15-28% by volume in air) of ammonia with a high lower limit (150,000 ppm) compared to conventional fuels. Furthermore, the absolute minimum ignition energy and auto ignition temperature is higher than conventional fuels. In addition, the toxicity limits of ammonia are far more severe than flammability limits making these limits less important. Nevertheless, ammonia is a flammable gas thus ignition sources should be kept away sufficiently in order to prevent fires. Furthermore, ammonia contains gas under pressure; may explode if heated. Thus, means for pressure relieve should be installed accordingly.

11.1.6.2 Toxicity

Ammonia is a gas at atmospheric conditions and highly toxic. Based on AEGL 3 exposure for 10 min to 2,700 ppm can be lethal. Therefore, adequate detection systems should always be present when handling and storing ammonia. In addition, means to cope with leakages are required to reduce the concentration for example with ventilation or dissolving ammonia with water spray. Alternatively, flaring could also be considered as an option for example for ammonia storage facilities in emergency conditions.

11.1.6.3 Environmental impact

As ammonia is highly toxic, spillage into the environment should be kept to a minimum. High concentrations of ammonia both in air and water can form a serious threat for all living organisms in its surroundings. Ammonia is part of the nitrogen cycle, both in air and water, so the environment can restore itself to its natural state with low levels of ammonia. Nevertheless, ammonia spillage can have long-lasting effects as restoration requires a significant amount of time depending on the extend of the spillage.

11.1.7 What risks are identified when using ammonia as a marine fuel?

Reflecting on the risk assessment the main specific risks of using ammonia as a marine fuel are ammonia exposure to humans and the environment. In addition, in the fuel supply system considered, the flammability risks of hydrogen, obtained from cracked ammonia, is present. Next to these unique risks the ammonia fuel system has similar risks like other fuel systems covering, unable to supply fuel, main engine failure, too high pressure of fuel supply, increase in temperature and pressure in system, unwanted continuation of flow and counter flow. Considering the vessel type, the inability to use boil-off as fuel is also an effect of the risks considered in the assessment.

11.1.8 What means are required to reduce the identified risks to an acceptable level, and how do they affect the design?

11.1.8.1 Risk mitigations

To safely handle ammonia (and hydrogen) as a fuel, spaces containing fuel lines should be equipped with ammonia (and hydrogen) detection combined with ventilation. Furthermore, in case of leakages remote operated shut-off valves should be installed to isolate the leakage and limit its impact. In line with this mitigation, redundancy in the fuel supply line should be arranged to ensure sufficient fuel supply for continuous operation in case part of the fuel supply is shut-off. In addition, in case of a blackout the main remote operated isolation valves should be installed with a fail close so when there is a loss of power the valves close automatically. As ammonia exposure to humans and the environment should be limited as much as possible, fuel lines should be routed with a sufficient distance from the shell, for example B/5 from the side. Where possible, fuel lines should be located in separate unmanned spaces. Where impossible, for example in the engine room, double-walled piping with pressure transmitters should be applied.

The ammonia fuel treatment room and similar to other fuel systems, the engine room, should be equipped with fire detection and a fire fighting system. Furthermore, to monitor the conditions of the fuel, pressure transmitters, temperature transmitters and flow detectors should be added. In addition, to cope with overpressure a pressure relieve system should be installed.

11.1.8.2 Design consequences and considerations

The main ship design consequences of the mitigations are on the arrangement due to the required separate spaces for the redundant fuel supply lines covering fuel trunks and fuel treatment rooms. Furthermore, the ventilation of the spaces containing fuel supply lines also require space for the intake and exhaust of air. The requirement of routing with sufficient distance from the side also impacts the effective use of available space of the vessel. All these factors increase the cost, especially the redundancy requirement. Therefore, implementation of 2 x 50% system capacity instead of 2 x 100% is considered to be important to limit these additional costs.

11.2 Recommendations

11.2.1 Internal combustion engine

11.2.1.1 Ammonia + Hydrogen

This project based the performance comparison of ammonia as a marine fuel on literature research and preliminary design calculations. The ammonia ICE option is selected to be the best solution for this project. Therefore, it is recommended to further investigate combustion of ammonia hydrogen mixtures in marine engines to obtain a more accurate view on performance like efficiency, load response, NO_x emissions, fuel slip and several others as a function of ammonia hydrogen mixture composition. Especially NO_x emissions deserve additional attention as much is still unknown about

ammonia hydrogen combustion in low speed two stroke marine engines. Based on literature study it was assumed that ammonia hydrogen combustion has similar NO_x emissions as HFO combustion in low speed two stroke marine engines. The higher nitrogen content in the ammonia hydrogen mixture, which would suggest that there are more NO_x emissions, is compensated by multiple aspects. These include: no “diesel dilemma” and thus freedom to cool peak temperatures, lower average temperature, homogenous charge of fuel air mixture and possibly SNCR, which is still unconfirmed. To what extent cooling of peak temperatures is desired is of particular interest. Although this could reduce NO_x emissions, it could also reduce the efficiency. Thus, it is recommended to further investigate ammonia hydrogen combustion in marine engines.

11.2.1.2 Ammonia + Marine Diesel

To realise ammonia as a marine fuel a step wise implementation could accelerate the application of ammonia as a marine fuel with in the first stage ammonia with marine diesel as a pilot fuel in an (CI) ICE. The second stage is an ICE using ammonia hydrogen mixtures followed by the third and final stage an SOFC using ammonia. Evaluating the first step, using ammonia with diesel in an (CI) ICE offers several benefits. Using ammonia with diesel in an (CI) ICE enables operators to significantly reduce harmful emissions. In addition, it provides the same certainty and reliability for continued operation, as in case the ammonia fuel system would fail, the operator can switch back to 100% diesel. Using ammonia with diesel in an ICE allows the operator to select the amount of ammonia himself. This offers flexibility to cope with ever changing economic viability to comply with harmful emission reduction regulations in the coming decades. Furthermore, the ammonia fuel system will be less expensive as redundancy of ammonia fuel supply is not required when using redundant diesel fuel supply. Therefore, it is also recommended to further investigate marine ICEs using ammonia and marine diesel.

11.2.2 Fuel cells

As fuel cell technology is still undergoing a lot of development it is recommended to maintain an accurate view on the technical and economic performance. Fuel cells might not power vessels today, but with its implementation ongoing in cars, buses, light trains and submarines they could become feasible for vessels for main power generation in the future. The SOFC seems particularly interesting as it can reach high efficiencies and is capable of handling multiple fuel types. Furthermore, the first application of fuel cells seems most preferable in ships which already have fuel-electric configurations. Therefore, it is recommended to further investigate the application of fuel cells in vessels, especially the SOFC and vessels which already have fuel-electric configurations.

11.2.3 Safety

The developed ammonia fuel system is based on the assumption that there is zero leakage in normal operational conditions. In practice this is not completely valid. For example, when the ammonia fuel system is shut down and the valves are closed, small amounts of gas could leak through a valve. This could cause a slow pressure build-up of ammonia in the fuel supply line towards the engine. To prevent this a block and bleed system after an isolation valve can be applied. Once the system is shut down the bleed valve, connected to the vent system, opens and the block valve closes. The bleed valve allows the minor amount of gaseous ammonia to be vented where the block valves prevents it from going further into the system. Multiple of these examples can be considered. Therefore, further analysis is considered to be required without the zero leakage assumption to continue the development. This should be further investigated and could be done with for example a quantitative safety analysis.

Hazardous areas of ventilation exhausts of spaces containing ammonia fuel lines should be determined by means of additional investigation. In addition, the hazardous area of the vent mast should be reviewed with the addition of the pressure relieve system of the ammonia fuel system. Furthermore, measures to monitor flow/activity of the vent mast including mitigation of ammonia ventilation either by water spray or flaring should be reviewed.

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As an ammonia carrier is used for the ammonia fuel system the main issue of ammonia fuel storage is not addressed as it was covered by existing regulations. Therefore, it is recommended to further investigate ammonia fuel storage so it can be applied on other ship types as well.

11.2.4 Closing statement

Overall, it can be stated that this research is a valuable first step towards the application of ammonia as a marine fuel. Yet a lot of additional research is still required to explore its full potential and feasibility.

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