The potential of ammonia as an alternative fuel in the marine industry

Marijke Kommers
4227123
SDPO.21.015.m

The potential of ammonia as an alternative fuel in the marine industry

by

M.Y. Kommers

Thesis for the degree of MSc in Marine Technology in the specialisation of Maritime Operations and Management

performed at

Delft University of Technology
Date of Exam: July 7, 2021

Thesis Committee
Dr. ir. J.F.J. Pruyn
Dr. ir. Lindert van Biert
Ir. J.J. Zwaginga

Author Details
Study number: 4227123

Preface

Last summer I was taken in total awe by the book *ready player one*. This book depicted a future world where human kind has used all resources and the world was left in a major energy crisis. People left cars with keys in the contact behind because there was no fuel available anymore. The world was shocked every other month with a new global pandemic and the majority of the people were struggling with famine and poverty. This book was written in 2012 and depicted the world in 2044. The chance of the world deteriorating with such a high rate is rather small but it did have an important message. If we don't change the way we consume and use, the world could face a substantial energy crisis. The subject of sustainability and global warming is of increasing importance. When this subject for a thesis came across, I was immediately interested and I have worked with enthusiasm on the subject of alternative fuels.

While writing this thesis I have learnt even more than during my studies. Not only the subject and research side of the process but also the process itself. I found it quite difficult to work on such a large project on my own and struggled to bring order in the chaos that I created. It took me a while to figure out which way the research was going. The information was gathered, but the framework was still missing. I mostly missed the surroundings of other students working on similar projects, due to working mostly at home due to the corona crisis. In the end I luckily found a good rhythm and I am happy with the result of this thesis.
The writing of this thesis was a challenging process which I wouldn't have been able to complete without the help of others. First of all, I would like to thank Jeroen Pruyn for his guidance during my research. The biweekly meeting were not only very helpful to give direction to the research but often also functioned as a motivational moment.
Next I want to thank my father Jef Kommers for always having a listening ear, technical eye and very helpful insight in the marine industry. Without my dad's help this thesis would lack the final technical touch in knowledge as well as English writing. Apart from helping with this thesis, my dad has been an important influence in my life and the choice for engineering. His enthusiasm for technique is unlimited and his work ethic is one I admire most. From him and my grandfather I inherit the passion for ships and engineering. A special thanks to my mum, sisters and grandma for always being there for me and have a listening ear when I struggled with the process.
Finally, I would like to thank my friends. In particular my best friend Megan, for lending her office to me and supporting me through the process. Also a big thanks to Bregje, who helped visualising certain aspects and helped the cover of this report. And finally, my roommates Emma and Imke, who have cooked and cared for me during deadline season.

Marijke Kommers
Rotterdam, June 2021

Summary

The current path the marine industry is following, the goals of the Paris Agreement to reduce emissions, will not be met. The marine industry is mainly sailing on HFO and emits 2.2% of the global greenhouse gasses (GHG) by doing so, as well as 18-30% of NO_x, 5-8% SO_x and 11% particulate matter (PM). The IMO has even predicted that the emissions of GHG will increase between 50 and 250% if the shipping industry continues on this path. In order to reduce emissions, the International Maritime Organization (IMO) has implemented ambitious goals for the next decades. However, the current policy measures sparks low ambition to meet this IMO GHG strategy. To be able to meet this goals, four options with different potential of reducing emissions are available, viz. efficient ship hull designs (20%), energy efficient engines (10-15%), more efficient propulsion (5-20%), clean technologies such as fuel cells and the use of alternative fuels (100%). Since the alternative fuel option has the largest potential in reducing emissions, a number of researched have looked into possible options for alternative fuel, such as LNG, LPG, methanol, biofuel, hydrogen and ammonia. This thesis looks into the potential of ammonia as an alternative fuel in the marine sector by 2030 by looking into the critical success factor for the fuel.

This research takes all the aspects of the marine industry into account and researches the mutual interaction and relation between the aspects. The main aspects are the power generation options, the fuel availability including the port logistics, price of the fuel, operations (OPEX), impact on the vessel (CAPEX) and legislation and rules. These aspects have a number of inter-dependencies.

The barrier related to the power generation option is the lack of availability of an engine that can run on ammonia. This engine needs to comply with legislation, which is not implemented yet. The barrier related to the fuel itself is the availability of the fuel in both volume and location. The production capacity is not yet at a level to fuel a significant part of the marine sector. The barrier related to the port are the logistics of the supplier and storage and handling of ammonia. Ammonia is a toxic substance and requires safety measures. These rules have not been implemented either. Closely related to the availability of the fuel is the price of the fuel. This is dependent on the demand of ammonia, which is currently zero for the marine sector. For the operational aspect is the lower energy density compared to conventional fuel an important barrier. For the same energy output, a greater volume of fuel is needed. This requires either extra stop overs during the voyage or a larger fuel tank, which could lead to loss of cargo space. The larger fuel tank has an impact on the design of the vessel, as well as the different storage and handling of ammonia compared to conventional fuels. Together with the legislation, this is an important barrier for the CAPEX of the vessel. This is a very important decision factor for the ship owner. Finally, most important barriers is the legislation. This aspect has the largest influence on all the other aspect and can promote other aspects to invest in ammonia and take steps in implementation. The regulation for sailing on ammonia are not yet in place. The IMO is responsible for the IGC and IGF code that regulate fluids as cargo and as fuel. The IMO has not started working on implementing ammonia as a fuel yet, since the demand of the fuel is currently low. This is however due to the regulations not yet being in place. Ship owners are reluctant to switch to another fuel when the risk of implementing the rules incorrectly are too large. The design requirements are not yet clear and it would be too costly to refit a vessel to the correct requirements for the early adaptors. Another aspect the regulations have large impact on are the engine options. Ammonia has a narrow flammability and is more difficult to ignite compared to conventional fuels. The design of the engine needs to comply with the regulations for safe ignition.

Contents

List of Figures ix

List of Tables xi

1 Introduction 1

2 Background information 3
- 2.1 Emissions . . . 3
- 2.2 IMO . . . 4
- 2.3 International regulations . . . 8
- 2.4 Current trajectory . . . 10
- 2.5 Alternative fuels . . . 11
- 2.6 Ammonia . . . 17
- 2.7 Researched potential . . . 19
- 2.8 Conclusion . . . 20

3 Problem definition 23

4 Methodology 25
- 4.1 Gap in research . . . 25
- 4.2 Scope . . . 25
- 4.3 Barriers . . . 26
- 4.4 Model . . . 30

5 Power plant configuration 35
- 5.1 Operational profile . . . 35
- 5.2 Power generation . . . 36
- 5.3 Impact on design . . . 44
- 5.4 Toxicity . . . 45
- 5.5 Codes and regulations . . . 45

6 Routing 49
- 6.1 Trade routes . . . 49
- 6.2 Case study . . . 51

7 Ports 55
- 7.1 Location and infrastructure . . . 55
- 7.2 Handling and transport of ammonia . . . 56
- 7.3 Policies . . . 56
- 7.4 Conclusion . . . 56

8 Production 59
- 8.1 Production . . . 59
- 8.2 Location and transportation . . . 65
- 8.3 Fuel price and costs . . . 66

9 Results 73

10 Conclusions 77

Bibliography 79

A Overview world fleet 85

B Import and export ports ammonia 87

List of Figures

2.1 SO_x and PM limits in and outside emission control areas [57] . . . 6
2.2 NO_x limits [56] . . . 6
2.3 Current and future emission control areas . . . 6
2.4 Past and future marine fuel demand [26] . . . 7
2.5 Fuel barrier dashboard [28] . . . 14
2.6 Comparing ammonia to other renewable fuels [24] . . . 14
2.7 Comparison of gravimetric and volumetric storage density of fuels [28] . . . 15
2.8 Bunkering intervals of alternative fuel options [28] . . . 16
2.9 Pathway 1 with focus on design requirements [28] . . . 17

4.1 Model with all aspects and their mutual interaction and relationship . . . 26
4.2 Material and energy flows in PFP system [32] . . . 33

5.1 Engine options [24] . . . 37
5.2 Layout layered PEMFC [60] . . . 40
5.3 Road map ammonia development project MAN [43] . . . 42
5.4 Ammonia drive system lay-out [23] . . . 43
5.5 Block diagram ammonia LFSS [43] . . . 43
5.6 Ammonia fuel tank options [43] . . . 44

6.1 Left:Global ammonia trade in August 2020 [43]. Right: Container ship trading routes [82] . . . 49
6.2 Bulk carrier routes; top left coal, top left and bottom left grain and bottom right iron ore [2] . . . 50
6.3 Worldwide ammonia ports [25] . . . 51
6.4 Three capacities for ammonia carriers [24] . . . 51
6.5 Most common bulk carriers sizes [69] . . . 52
6.6 Engine volume [60] . . . 53

8.1 Production of green ammonia [36] . . . 60
8.2 Production of ammonia per region [43] . . . 62
8.3 Projected annual ammonia production [43] . . . 63
8.4 Pathway to green ammonia [43] . . . 64
8.5 chemical reaction in SOFC and SOEC [71] . . . 65
8.6 Area required to produce 30% of global marine fuel demand with wind power [43] . . . 65
8.7 Ammonia import and export in 2017 [25] . . . 66
8.8 Market prices estimation for different classes of ammonia [43] . . . 67
8.9 Estimated production cost and market price of conventional and blue ammonia [43] . . . 68
8.10 Estimated production cost of green ammonia [43] . . . 69
8.11 Break even price of hybrid green ammonia [43] . . . 69

A.1 Overview of world fleet in 2015 [62] . . . 85

B.1 Terminals in Asia and Oceania . . . 87
B.2 Terminals in Baltic . . . 88
B.3 Terminals in Mediterranean . . . 88
B.4 Terminals in Middel East . . . 89
B.5 Terminals in South America . . . 89
B.6 Terminals in North America and Caribbean . . . 90

List of Tables

2.1 Summary international regulation . . . 7
2.2 EU GHG emission reduction targets . . . 8
2.3 Summary EU regulations . . . 10

4.1 Interdependency matrix of the barriers . . . 28
4.2 Volumetric energy demand . . . 31
4.3 Volumetric space available . . . 31
4.4 Range attainable . . . 32

5.1 Amount of container vessels per gross tonnage . . . 36
5.2 Amount of bulk carriers per gross tonnage . . . 36

6.1 Top trade routes in 2017 . . . 50
6.2 Container vessel sizes . . . 52
6.3 Case ships . . . 52
6.4 Results Emma Maersk . . . 54
6.5 Attainment rate Emma Maersk . . . 54
6.6 Attainment rate case vessels sailing on ammonia . . . 54

8.1 Production levels ammonia in million tons . . . 63
8.2 Ammonia prices estimations in USD/mt . . . 67
8.3 Investment costs in million USD for conversion versus new build . . . 70

Nomenclature

Abbreviations

AFC	-	Alkine fuel cell
AIS	-	Automatic identification system
Capex	-	Capital expenditure
CCS	-	Carbon capture and storage
CH_4	-	Methane
CI	-	Compression ignition
CO_2	-	Carbon dioxide
ECA	-	Emission Control Areas
EEDI	-	Energy Efficiency Design Index
ETS	-	Emission trading system
FQD	-	Fuel Quality Directive
GDP	-	Global economic growth
GHG	-	Greenhouse gas
H_2	-	Hydrogen
H_2O	-	water
HB process	-	Haber-Bosch process
HCCI	-	Homogeneous charge compression ignition
HEMFC	-	Hydroxide exchange membrane fuel cell
HFO	-	Heavy fuel oil
HSFO	-	High-sulphur fuel oil
HVO	-	Hydrotreated vegetable oil
ICE	-	Internal combustion engine
IGF code	-	International code of safety for ships using gases or other low-flashpoint fuel
ILUC	-	Indirect land use change
IMO	-	International Maritime Organization
ISPT	-	Institute for Sustainable Process Technology
LBG	-	Liquefied biogas
LNG	-	Liquid natural gas
LPG	-	Liquid petrol gas
MARPOL	-	International Convention for the Prevention of Pollution from Ships
MBM	-	Market based measure
MCDA	-	Multi-criteria decision analysis
MDO	-	Marine diesel oil
MEPC	-	Marine Environment Protection Committee
MGO	-	Marine gas oil
MVR	-	Monitoring, reporting and verification of emissions
NECA	-	Nitrogen Oxide Emission Control Area
N_2	-	Nitrogen
N_2O	-	Nitrous oxide
NH_3	-	Ammonia
NO	-	Nitric oxide
NO_x	-	Nitrogen oxides
NREAP	-	National Renewable Energy Action Plan

O_3	-	Ozone
ODS	-	Ozone depleting substance
Opex	-	Operating expenditure
PEMFC	-	Proton exchange membrane fuel cell
PFP	-	Power-to-fuel-to-power
PM	-	Particulate matter
PRD	-	Pearl River Delta
ppm	-	Parts per million
RED	-	Renewable Energy Directive
SAVE model	-	Systematic assessment of vessel emission model
SECA	-	Sulphur emission control area
SEEMP	-	Ship Energy Efficiency Plan
SI	-	Spark ignition
SO_2	-	Sulphur dioxide
SO_3	-	Sulphur trioxide
SO_x	-	Sulphur oxides
SOFC	-	Solid oxide fuel cell
SPB	-	San Pedro Bay
STS	-	Ship-to-ship
ULSHFO/VLSFO	-	Ultra low sulphur heavy fuel oil/ very low sulphur fuel oil
VOC	-	Volatile organic compounds

Symbols

η	-	Efficiency
D	-	Volumetric density in kg/m^3
E	-	Energy in kWh
P	-	Engine power in kW
R	-	Range of ship in nautical miles
V	-	Volumetric energy demand in m^3
v	-	Vessel's speed in nautical miles per hour or knots

1
Introduction

The marine industry is after the airline industry the most difficult industry to make sustainable. The industry consumes yearly approximately 330 million tons of fuel. Most vessel sail on cheap heavy fuel oil (HFO) which is very polluting. Especially nowadays with a low oil price the choice for HFO is often made [29]. However, the importance of sustainability is becoming increasingly urgent due to the size of the marine industry. The shipping market is a significant market in the world economy and is responsible for transporting roughly 90% of all goods globally. The shipping industry is the cleanest way to transport goods, but still is responsible for emitting around 940 million tonnes of CO_2 annually and is responsible for 2.2% of the global greenhouse gas (GHG) emission [58]. Besides transporting goods the maritime industry is also operating offshore, for example with pipe laying and deep sea operations, which also emits a significant amount of greenhouse gases. According to a study from IMO the emission of GHG will increase between 50 and 250% if the shipping industry stays on this path [51]. Besides the emission of GHG, the shipping industry is responsible for emitting 18-30% of NOx [61], 5-8% SOx [84] and 11% particulate matter (PM) of the global air pollutants [89]. New rules and regulations about the reduction of GHG emissions are set in place by the IMO and international governments to prevent this scenario. These rules and regulations are discussed in chapter 2.

There are a number of technical possibilities for emission reduction in marine transportation. The most common options are more efficient ship hull designs, energy efficient engines, more efficient propulsion, clean technologies such as fuel cells and the use of alternative fuels [6]. Due to increasing environmental responsibilities in the marine industry, multiple researches are launched to find an alternative fuel with less emission of green house gases and air pollutants. Multiple alternatives for HFO are available, such as LNG, LPG, methanol, biofuel, hydrogen and ammonia. The fossil based alternatives have a GHG reduction of approximately 20% [27], but the other options provide an even better solution to the GHG emissions. This research focuses on the potential of ammonia as an alternative fuel.

In order to implement a new fuel, it has to comply with a number of requirements. It needs to be available, be cost effective, compatible with current and/or future technologies and comply with environmental requirements. These requirement form barriers in the way of implementation and are closely connected to each other. To be able to implement an alternative fuel successfully, all these barriers need to be overcome. This thesis looks into the critical success factors of implementing ammonia as an alternative fuel and what the critical path is in doing so. Chapter 2 first gives an overview of the current and upcoming regulations to which the marine sector needs to comply. This is followed by an introduction of a number of alternative fuel options and how these compare to each other, and mainly to ammonia. Chapter 3 introduces the research questions and chapter 4 discusses the gap in research and the model that is used to answer the research questions. The chapters 5, 6, 7 and 8 are then used to find the variables needed in the model.

2
Background information

This chapter gives background information over the reason for the research of alternative fuel by looking into the rules and regulations that are put in place by IMO and national governments regarding emission of greenhouse gasses and air pollutants. It is clear that alternative fuels are a promising solution to the GHG emission problems and ammonia is introduced as an potential fuel. After discussing all aspects connected to ammonia, the research done so far is discussed, including comparing ammonia to other alternative fuels.

2.1. Emissions

As mentioned in the introduction global warming is still an important topic globally. The emission of harmful fumes and air pollutants is still causing disruption of the ecosystem and climate change. The gasses emitted by burning fuel are Greenhouse gasses (GHG), NO_x, SO_x and Particulate Matter (PM).
Greenhouse gasses (GHG) consist out of Carbon dioxide (CO_2), water vapour (H_2O), methane (CH_4), nitrous oxide (N_2O) and ozone (O_3). The impact of GHG is for over 90% from CO_2 and CH_4 emission mainly results from burning fossil fuels. The GHG emissions have a significant impact on global warming and all the additional problems, such as extreme weather, withdrawal of glaciers and ice fields, increased water evaporation (droughts) and melting permafrost. These aspects have a global temperature rising as a consequence [74]. Research predicts that a rise of 2°C causes an increase in extinction of plants and animal species, shifts in patterns of agriculture and a rising sea level. The shipping industry is responsible for 2.2% of the global GHG emissions [58].
NO_x is a collective name for nitrogen dioxide (NO_2) and nitric oxide (NO). When NO_2 reaches the lungs it converts into nitrous and nitric acid which are highly irritating and causing damage to the lungs. Exposure of 0.06-0.1 ppm NO_2 for two years can lead to acute respiratory disease. NO is not considered a hazard to health, but during combustion it reacts with oxygen to form NO_2, which is hazardous. The shipping industry is responsible for 18 to 30% of the global NO_x emission [61].
SO_x is a collective name of sulphur dioxide (SO_2) and sulphur trioxide (SO_3). SO_2 contributes to acid deposition which can lead to changes in soil and water quality. Reports have shown that annually 11.3 million tonnes of SO_2 is emitted by the maritime transport industry [44], which is approximately 5-8% of the global emissions [84].
Particulate matter (PM) is the collective name of particles less than 2.5 micrometers in diameter. Long term exposure can lead to cardiopulmonary disease (better known as heart-lung disease) and reduce life expectancy. In 2013 shipping contributed for 11% to the emission of PM. Close to port this percentage can even go up to 15%. The other means of transport that contributed are road transport (12%), aviation (1%) and rail transportation (0%) [10].

It is clear that the shipping industry needs to become more sustainable. However, shipping companies are not likely to invest in clean solutions since they want also to remain profitable. The only way to make the industry more sustainable is to implement rules and regulations. The next sections describe the rules and regulations enforced on international and local level [28].

2.2. IMO

Shipping is a global business which is responsible for 80% of the global trade and therefore, only local government legislation and regulations are not enough. International rules are needed to reduce emissions everywhere. The International Maritime Organization is a separate body of the United Nations that is responsible for the safety and security of shipping and the prevention of marine and air pollution by ships. The IMO sets a regulatory framework for the industry obliging companies to invest in safety, security and environmental performance. The measures include all aspects of international shipping, such as ship design, construction, equipment, manning, operation and disposal. As part of the United Nations the IMO contributes to the 2030 Agenda for Sustainable Development and the associated Sustainable Development Goals. This plan aims to eradicate poverty, create a healthier planet and a more just world. Most goals on the agenda will only be met if the supporting transportation systems become more sustainable [58].
The Third IMO GHG study of 2014 estimates the emission of the international shipping industry in 2012 at 796 million tons CO_2. This accounts for 2.2% of the total global anthropogenic (caused by human activity) CO_2. The expected growth of GHG emissions lies between 50 and 250% by 2050, mainly due to the growth of the maritime trade worldwide. IMO has added a new chapter to the MARPOL Annex VI to further enhance ship's energy efficiency and develop measures to reduce emission of greenhouse gasses.

MARPOL Annex VI

The International Convention for the Prevention of Pollution from Ships (MARPOL) Annex VI sets a limit for the main air pollutants from ship's exhaust gas, such as sulphur oxides (SO_x) and nitrogen oxides (NO_x). It also prohibits emissions of ozone depleting substances (ODS), on board incineration and emissions of volatile organic compounds (VOC) from tankers [55]. The MARPOL rules were reinforced in 2005 by the Marine Environment Protection Committee (MEPC) with stricter limits since the technology and implementation has improved significantly. This was again done in 2008 with the addition of the NO_x Technical Code 2008, enforced in 2010. The changes included a significant reduction in the global emissions of SO_x, NO_x and particulate matter and the introduction of emission control areas. The MARPOL Annes VI further consists of two main measures, the Energy Efficiency Design Index (EEDI) and the Ship Energy Efficiency Plan (SEEMP). Both measures are discussed in the next sections.

Energy Efficiency Design Index

Even though ships are the most fuel-efficient mode of bulk transportation, in 2009 the Second IMO GHG study discovered a significant potential in improving the energy efficiency by using more efficient engines and propulsion systems. This would lead to less fuel consumption and a reduction in CO_2 emissions [50]. To stimulate this process the Energy efficiency design index (EEDI) requires new ships to comply with a minimum mandatory energy efficiency performance level per capacity mile. The aim is more energy efficient and less polluting equipment on board of ships. The required level depend on the date of built, type of ship and ship size. In order to stimulate developments towards cleaner shipping, the reference value is tightened in three steps since its introduction (in 2015, 2020 and 2025). Each step is a 10% reduction of CO_2 emission relative to the reference level of the ships build between 2000 and 2010. The EEDI is set in place for tankers, bulk carriers, gas carriers, general cargo ships, container ships, refrigerated cargo carriers and combination carriers, since these ship are the largest and most energy intensive of the world merchant fleet. Since 2014 is the EEDI expanded to LNG carriers, ro-ro cargo ships, ro-ro passenger ships and cruise passenger ships with non-conventional propulsion. With this amendment the EEDI now covers 85% of the CO_2 emissions from international shipping [49]. How the limit is met is up to the ship owner. The choice of equipment is free as long as the required energy efficiency level is met. The index can be expressed as the vessels' specific ratio between the impact to the environment and the benefit for the society, or put in other words: the ratio between CO_2 emissions and transported goods. The EEDI provides a specific amount of grams CO_2 per ship's capacity-mile that an individual ship design is allowed to emit.

$$EEDI = \frac{Impact\ to\ the\ environment}{Benefit\ for\ society} = \frac{CO_2\ emissions}{Transported\ goods} \tag{2.1}$$

Ship Energy Efficiency Management Plan

The Ship Energy Efficiency Management Plan (SEEMP) focuses on improving the energy efficiency of new and existing vessels. The SEEMP does not make a distinction between type of ship but is applicable for all ships above 400 GT. The SEEMP uses operational measures such as weather routing, trim and draught optimisation, speed optimisation and just-in-time arrival in ports. In 2016 the MEPC added rules for 5,000 GT ships to collect and submit fuel oil consumption data, which have been in force since 2019 [53].

Green House Gas Reduction

The MEPC approved a plan in 2018 for the reduction and eventually phasing out of greenhouse gas emissions. This plan included more GHG studies and a three step plan to improve ship energy efficiency. The steps are listed below [54].

- **Further reduction of carbon foot print of ships** by implementing further phases of the EEDI for new ships.
- **Decline of carbon intensity of international shipping** by reducing the average CO_2 emissions per transport cargo across the international shipping industry. The reduction should be at least 40% in 2030 and the aim is for a 70% reduction by 2050 compared to the 2008 levels.
- **GHG emissions peak and decline**, meaning the peak should be reached as soon as possible and a decline is only to follow. The reduction of the total GHG emission should be at least 50% by 2050 compared to the 2008 levels. The ultimate goal is to phase out GHG all together. This is part of the Paris Agreement temperature goals.

This plan has led to short-, mid- and long-term measures in order to reach the set goals. The following measures are part of the plan:

- **Strengthen EEDI requirements** for some categories of new ships. Described in section 2.2
- **Inventory of the global emission of GHG** from international shipping between 2012 and 2018 as well as an estimate of the carbon intensity of the global fleet in the same period. Additionally an inventory of the year 2008 to set a base case. The next step is setting up scenarios for future international shipping emission between 2018 and 2050.
- **Cooperation between port operations and shipping industry to reduce GHG emissions** by promoting actions in the port sector. This includes development of shore power supply (which is accepted as a source of renewable energy), provision of bunkering of alternative low-carbon and zero-carbon fuels, promoting sustainable low-carbon emissions for shipping and optimisation of port calls, such as just-in-time arrival of ships.

Emission Control Areas

The Emission Control Areas (ECA's) are designated areas near coast lines where the IMO has set stricter rules concerning emissions from vessels. The ECA's have three different levels, tiers I through III. The tiers are designed to reduce NO_x, SO_x, ODS and VOC emissions from marine diesel engines.

SECA

The sulphur limits inside and outside the Sulphur Emission Control Area (SECA) are shown in figure 2.1. For SECA the engines installed between 1 January 1990 and 1 January 2000 need to comply with Tier I. This limits the sulphur to 1.5% m/m. Tier II includes a reduction of emissions from marine diesel engines installed between 1st of January 2011 and 1st of January 2015. The sulphur limit here is 1.0% m/m. Tier III is a more stringent emission limit for engines installed after 1 January 2016 in the areas North American Emission Control Area and the U.S. Caribbean Sea Emission Control Area. Tier III would also apply for future ECA zones. The areas under evaluation are shown in figure 2.3 where dark green areas represent the existing ECA's and the light green mark potential future zones. The Tier III rules are only applicable for ships larger than 500 GT and over 24 meter in length. Recreational ships don't have to meet the requirement. The sulphur limit here is 0.1% m/m [55][57].

NECA

The Nitrogen Oxide Emission Control Area (NECA) sets limits for installed marine diesel engines with an output larger than 130 kW. The tonnage of the ship is irrelevant. Figure 2.2 shows the three tiers and the limits the ships need to comply with. As can be seen in the figure the total weighted cycle emission limit is dependent on the construction date and the rpm of the engine.

Outside an ECA established to limit SOx and particulate matter emissions	Inside an ECA established to limit SOx and particulate matter emissions
4.50% m/m prior to 1 January 2012	1.50% m/m prior to 1 July 2010
3.50% m/m on and after 1 January 2012	1.00% m/m on and after 1 July 2010
0.50% m/m on and after 1 January 2020*	0.10% m/m on and after 1 January 2015

Figure 2.1: SO_x and PM limits in and outside emission control areas [57]

Tier	Ship construction date on or after	Total weighted cycle emission limit (g/kWh) n = engine's rated speed (rpm)		
		n < 130	n = 130 - 1999	n ≥ 2000
I	1 January 2000	17.0	$45 \cdot n^{(-0.2)}$ e.g., 720 rpm – 12.1	9.8
II	1 January 2011	14.4	$44 \cdot n^{(-0.23)}$ e.g., 720 rpm – 9.7	7.7
III	1 January 2016	3.4	$9 \cdot n^{(-0.2)}$ e.g., 720 rpm – 2.4	2.0

Figure 2.2: NO_x limits [56]

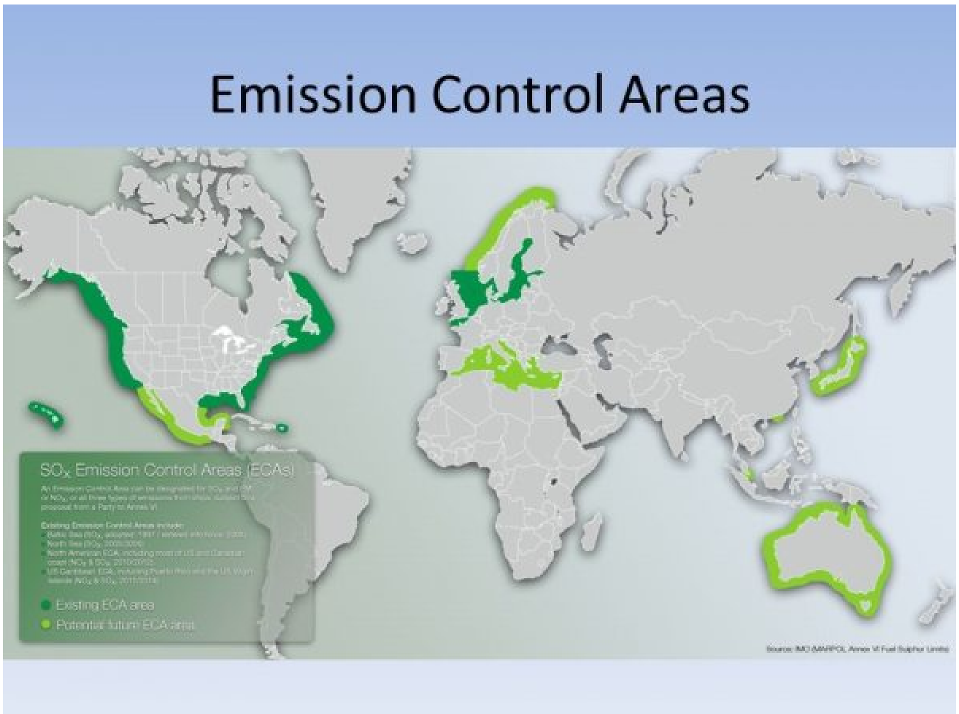

Figure 2.3: Current and future emission control areas

Sulphur norm

Besides the sulphur cap in the ECAs, a global sulphur cap is set in place in order to reduce the sulphur limit from 3.5% to 0.5% for deep sea sailing since the 1st of January 2020. To comply with the norm often scrubbers are installed to be able to continue sailing on high-sulphur fuel oil (HSFO). Alternatively ship owners chose to use Ultra Low Sulphur Heavy Fuel Oil (ULSHFO/VLSFO), Liquid Natural Gas (LNG) or blends of Heavy Fuel Oil (HFO) and Marine Gas Oils (MGO) (distillate in figure 2.4) to meet the requirements. Figure 2.4 shows a predicted shift in fuel choice as from the year 2020. ULSHFO contains <0.1 % sulphur and it is believed that more owners will shift towards this fuel to comply with the regulations. These fuels all result in a reduction in sulphur emissions and LNG also reduces the emission of NO_x and Particulate matter (PM). However, the reduction of emitted greenhouse gasses is minimal and these fuels will not achieve the applicable norms [85]. One party, however, expects a sharp price spread between low-sulphur and high sulphur fuel in the bunker market post 2020. This will drive to a strong uptake in scrubbers. This entails an increase in HFO in favour of VLSHO, since VLSHO is more expensive [48].

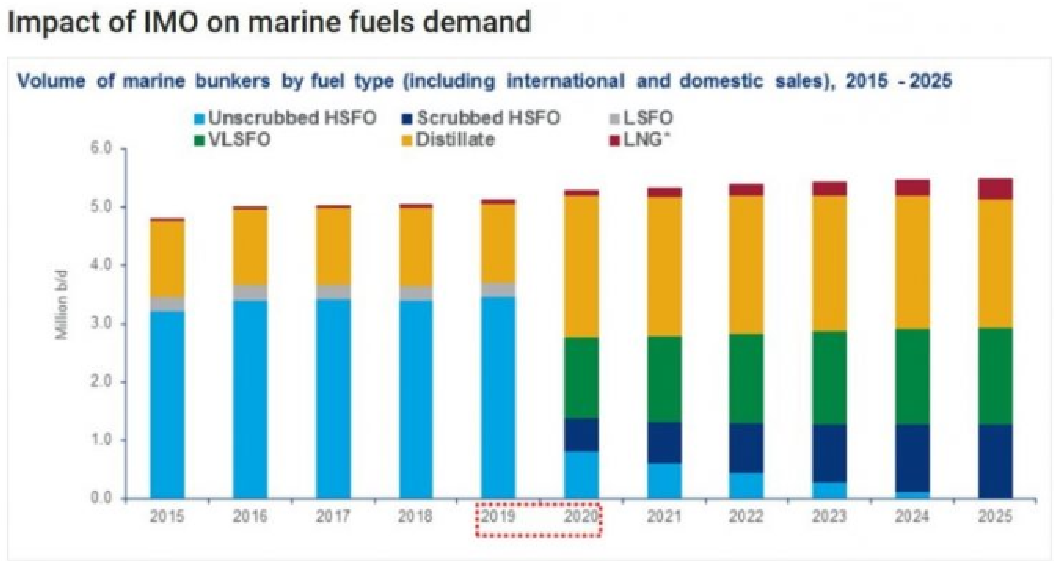

Figure 2.4: Past and future marine fuel demand [26]

Conclusion IMO rules and regulations

The table 2.1 summarises all the rules from IMO in the MARPOL Annex VI.

Policy	Effective since	Regulation
ECA Tier 1	2005	Marine diesel engine installed between 1990 and 2000 Sulphur limit of 1.5 % m/m
ECA Tier 2	2005	Marine diesel engine installed between 2011 and 2015 Sulphur limit of 1.0 % m/m
ECA Tier 3	2010	Marine diesel engine installed on or after 1 January 2016 operating in North American ECA and the U.S. Caribbean Sea ECA Marine diesel engine installed on or after 1 January 2016 in future ECA Sulphur limit of 0.1% m/m
ECA	2015	SO_x and PM reduced to 0.10%
EEDI	2015	10% CO_2 reduction relative to ships build between 2000 and 2010
EEDI	2020	20% CO_2 reduction relative to ships build between 2000 and 2010
EEDI	2025	30% CO_2 reduction relative to ships build between 2000 and 2010
SEEMP	2019	All ships > 5000 GT collect and submit fuel oil consumption data
GHG reduction	2018	- 40% CO_2 reduction by 2030 relative to 2008 levels - 70% CO_2 reduction by 2050 relative to 2008 levels - 50% reduction of all GHG emissions relative to 2008 levels
MARPOL Annex VI	2020	- Global sulphur limit from current 3.5% to 0.5% - Fuel oil standard of 0.5% sulphur limit

Table 2.1: Summary international regulation

2.3. International regulations

To provide a clear overview of all the rules and regulations concerning GHG, SO_x, NO_x and PM emissions the countries with the most bunker supplies are researched. The world counts approximately 400 major bunkering ports, but most demand is located in a few strategically located ports. These ports account for 60% of all bunker sales. The ports are located in Singapore, China, the USA, the UAE, the Netherlands and South Korea. The applicable regulations in these areas are discussed below. Regarding the situation in the Netherlands the whole EU is reviewed in order to get a broader understanding of the applicable rules and legislation [13].

EU regulations

The EU has set general emission reduction targets, shown in table 2.2. The 2020 climate and energy package is put in place in 2009 to ensure that the EU meets the climate and energy targets for the year 2020. The targets are 1) a 20% cut in GHG emissions relative to 1990 levels, 2) 20% of the energy used in the EU should be from renewable sources and 3) 20% improvement in energy efficiency. The EU has taken the following actions to meet the targets. The first action is the Emission trading system (ETS) that will reduce GHG emissions in the power and industry sector and the aviation sector which is responsible for 45% of the EU's GHG emission levels. The target is to reduce emissions by 21% relative to the 2005 level.
The second action is the National Emission Reduction target, which represents the balance of 55% of the EU emissions. This includes the housing, agriculture, waste and transport (except aviation) sector. The targets differ per country since it is dependent on national wealth. The richest countries are required to reduce 20% while the least wealthy country is allowed an increase of maximum of 20%.
The third action involves binding national targets for the share of renewable energy in the total consumption. These targets also depend on the countries starting point for production of renewable energy. For example Malta only has to have a 10% share but Sweden has a 49% share. The 20% overall target includes a 10% target in the transportation sector.
The shipping industry is currently not included in the targets due to the risk of losing its market share in the global industry. If the rules are too strict, ship owners are likely to divert their bunkering demands to less-legislated ports [65].

The 2030 climate and energy framework covers the period between 2021 and 2030. The targets are 1) a 40% reduction in GHG emissions relative to 1990 levels, 2) 32% of the energy used in the EU should be from renewables and 3) 32.5% improvement in energy efficiency. The 40% cut in GHG emissions will help to make the economy climate neutral and reach the goals of the Paris Agreement. To reach these goals the ETS sector has to reduce 43% of its emissions and the non-ETS sector has to reduce down to 30%, both relative to 2005 levels. The renewable energy share is increased from the original set point 27% to a 32% share. The energy efficiency factor is increased from the original target of 27% to 32.5% [66].

The objective of the long term strategy is to be climate neutral in 2050, meaning a net-zero GHG emission economy. By 2020 all parties have to state their long-term low GHG emission development strategy [67].

Policy	Time period	GHG emission reduction	Renewable energy share	Improvement in energy efficiency
2020 climate & energy package	< 2020	20%	20%	20%
2030 climate & energy framework	2021-2030	40%	32%	32.5%
2050 low-carbon economy	> 2031	Climate neutral	-	-

Table 2.2: EU GHG emission reduction targets

In 2011 the European Commission stated that the EU maritime transport should reduce its emissions by 40% by 2050 relative to the 2005 level by using alternative fuels and technology. In 2013 the European Commission decided to include the shipping emissions into the EU reduction targets. The process in split up into three phases.

- Monitoring, reporting and verification of emissions (MVR)
- Define reduction targets for maritime transport sector

- Application of a market based measure (MBM)

Progress is currently made in the first stage of monitoring, reporting and verification but no targets have been set and no measures have been taken. The MVR directs ships of 5000 GT and above that sail from and between ports of EU member states to report yearly CO_2 emissions. This is estimated to be 55% of all ships stopping in EU port and emit 90% of the CO_2 emissions. The monitoring is limited to the CO_2 emission since this contributes the main part of all GHG emissions and it reduces the administrative burden on ship-owners and operators. It is the same rule as the IMO has set, but it is a different report [27].

EU sulphur directive 2020

The Sulphur directive regulates the sulphur content of gas oils and heavy fuel oils in the EU. The sulphur content is restricted to 0.1% in the Sulphur Emission Control Areas (SECAs) since 2015 and 0.5% sulphur content in the EU water outside the SECAs since 2020 [22]. This regulation is the same as the IMO has set.

Fuel Quality Directive

The Fuel Quality Directive (FQD) requires fuel suppliers to reduce the greenhouse gas intensity by 6% by 2020 relative to the 2010 energy mix of 94.1 g CO_{2eq}/MJ [68]. In order to achieve this target the switch to biofuels, electricity, less carbon intense fossil fuels and renewable fuels of non-biological origin needs to be made. The FQD will only affect to the inland shipping sector since the requirement only apply to road transport and gas oil used in non-road-mobile machinery [27].

Renewable Energy Directive 2009

The EU has set up the Renewable Energy Directive (RED) to contribute to the GHG reduction. The RED is the main regulatory frame work for renewable energy in the EU. The goal is to get 20% of its energy from renewable sources by 2020, which includes 10% for transport. This target is EU wide, but every member sets its own target on basis of each particular situation, such as climate, agriculture, forestry, etc. Also the starting point and the potential of renewables is taken into account. This target and steps to reach the target are captured in a National Renewable Energy Action Plan (NREAP), which is member dependent and needs to be handed in every two years. Most member states have chosen to focus on biofuel in the NREAP.
Equation 2.2 is used to calculate the target. In this equation the denominator consists only of the fuels used in transport on road and rail. Shipping is not yet included, but would help reaching the targets.

$$\text{Target} = \frac{\text{Renewable transport fuel}}{\text{Total transport fuel}} \tag{2.2}$$

Additionally, the RED takes the technical, economic and environmental aspects of the production process into consideration. If the renewable fuel is produced with emissions in the process, these emissions are added to the total.

Renewable Energy Directive 2018

In the RED II the overall renewable energy resources consumption target by 2030 is increased from 27% to 32%. This updated plan includes a sub-target for the road and rail transport sector of 14% by 2030. The RED II also has stricter rules about what is a renewable resource and what is not. Biofuels are usually produced on cropland that has previously been used for other agriculture, such as growing food or feed. When the production of food and feed has to emigrate, it may lead to the use of non-crop land or high carbon stock land such as forest, wetlands and peat lands. This is called indirect land use change (ILUC). The release of CO_2 stored in trees and soil nullifies the greenhouse gas savings from the use of biofuel. Limits has been set to what extent high ILUC-risk biofuels, bioliquids and biomass can be used. Member states are allowed to use biofuels above the limit, but it doesn't count towards the renewable target. Since these rules apply on biofuels, this report will not research it further [38].

Emission Trading System

The EU Emission Trading System, ETS, works on a cap and trade principle. The cap is set for an installation on the total amount of GHG emissions that is allowed to be emitted. The cap is reduced over time to decrease total emissions. Installations buy or receive allowances and can trade these with other installations if needed.

If the installation exceeded the allowance, heavy fines are imposed. If an installation has spare allowances, it can either sell or keep them for next year. This is an effective tool that has reduced emissions with 35% between 2005 and 2019. The goal is an increase in the EU's net GHG emission reduction to at least 55% by 2030. The system operates in all EU countries plus Iceland, Liechtenstein and Norway and also includes the aviation sector for flight between airports in the European Economic Area. The marine sector is however excluded for this system [21].

Conclusion EU rules

The table 2.3 summarises the rules as stated by the EU in the RED I and RED II.

Policy	Goal date	Regulation
EU sulphur directive	2015	Sulphur limit 0.5% outside SECA, 0.1% inside SECA
Fuel Quality Directive	2020	Fuel suppliers reduce GHG intensity by 6% relative to 2010 energy mix, effective since 2017
Renewable Energy Directive I	2020	20% of energy from renewable sources, including 10% in transport, effective since 2009
Renewable Energy Directive II	2030	32% of energy from renewable sources, including 14% in transport, effective since 2018
European Commission	2050	Maritime transport should reduce emission by 40% relative to the 2005 levels, effective since 2011
EU Emission Trading System	2030	Increase in the EU's net GHG emission reduction of 55%, effective since 2005

Table 2.3: Summary EU regulations

Other locations

The rules and regulations of the IMO and the EU give a good overview of the rules that the marine sector needs to comply with.

2.4. Current trajectory

Under current policies the shipping industry will not meet IMO carbon reduction goals. The total emission level is still increasing, despite efficiency gains. In the time between 2013 and 2018 the total CO_2 emission has increased from 770 mt to 870 mt, an increase of 13%. In the same period the world seaborne trade increased from 50,500 to 60,400 billion tonne-miles, an increase of 20%. This indicates that sea trade has become more energy efficient. The monitoring, reporting and verification system (MRV) of the EU supports this claim. Ships built after 2013 are significantly more energy efficient than older ships. However, despite this energy efficiency, the growth of emissions will make it difficult to reach the IMO GHG reductions goals. Also, it is expected that the global demand for transportation by ship will increase with 39% by 2050. If this growth and the current applicable policies are continued, the emission levels will reduce by 27%, which is significantly less than the target of IMO. Carbon-neutral fuel should be 30 to 40% of the fuel mix in 2050 and energy efficiency should be improved in order to meet IMO GHG ambitions. To be able to meet the IMO targets, low and zero emission technology and application should begin on large ocean going ships in the near future since it is responsible for 80% of the world fleets emissions of CO_2.

There are multiple options to achieve this. The first one is in the logistic and digitalisation sector, which includes speed reduction, vessel utilisation, vessel size and alternative routes. This sector has a potential to reduce GHG emissions by approximately 20%. The second option is improving hydrodynamics with hull coating, hull-form optimisation, air lubrication and hull cleaning. The potential to reduce GHG emissions for this sector is 10 to 15%. The third sector is machinery, which includes machinery improvement, waste heat recovery, engine de-rating and battery hybridisation. This can reduce the GHG by 5 to 20%. The last sector, the fuel and energy source sector, has a potential of up to 100% [28]. The last sector is therefore most promising to look into.

Multiple researches have been performed on alternative fuels. It became clear that the level of readiness at this point of most alternative fuels is not sufficient to compete with traditional fuels. Only less than 1% of the world fleet is sailing on alternative fuels, which is mostly in the short sea segment and non-cargo ships. This has a very small impact on the total of marine emissions. The alternative fuels that currently are mostly used are still fossil based, such as LNG (159 ships in 2019). For new-build vessels an increase in LNG fuel system is expected in the next few years, as well as for batteries for full-electric and hybrid-electric operations. However, looking into the future, hydrogen is often named as the most sustainable option [70]. Another promising fuel is ammonia since it has a higher energy per volume than hydrogen and can be produced from green hydrogen in an accessible process [28]. The next section will make a comparison between alternative fuels.

2.5. Alternative fuels

The IMO GHG reduction strategy has an impact on shipping qua costs, asset values and earning capacity. What are the influential drivers and barriers to change to a new fuel and which fuel has the highest potential? The objective of alternative fuel options can be split into net GHG emissions and carbon footprint.

- **No carbon emissions at the stack**, such as electricity, hydrogen and ammonia, provided the production is also carbon neutral. The production should be based on renewable energy, nuclear energy and fossil energy with carbon capture and storage (CCS).

- **Carbon emissions at the stack**, such as biofuels and electro fuels. The condition is that the carbon contained in the fuel is sustainably sourced and which otherwise would have been part of the natural carbon cycle. This means that no more CO_2 will enter the atmosphere then as through the natural carbon cycle.

Both groups have a significant reduction in GHG, SO_x, NO_x and PM emissions. Regulations to reduce emissions are the initial drivers for ship owners to switch to alternative fuels. These alternative fuels, however, have other storage and engine requirements than conventional fuels. Together with availability of the fuel those are the main barriers for alternative fuels. The next section discusses the fuels LNG, methanol, biofuels, hydrogen, e-fuels and ammonia, and batteries as alternative energy source. Later on these options are compared to each other.

LNG

LNG has potential to reduce emissions and is priced competitively compared with conventional fuels. LNG results in a significant NO_x reduction and complies with the IMO NO_x Tier III limit. However, LNG also has a methane slip. LNG has a tank-to-propeller NO_x reduction of 20-24% compared to MGO, with the methane slip factored in. The emission of SO_x, PM and black carbon is significantly reduced or even eliminated.
Rules and safe design directive are put in place but on-board engine and storage technologies are more expensive than the alternatives that are currently used. Also, the capital costs must be reduced in order to improve competitiveness. The fuel price is somewhat competitive, but varies from time to time. A global market such as the fuel oils have, is not yet in place. The new-build price of a LNG vessel is about 10-30% higher than a diesel-fueled ship, recently around 20%. LNG fuel tanks require two to three time as much volume compared to MDO for the same amount of energy. These extra costs should be compensated with reduced operational expenditure, which is dependent on fuel price and maintenance costs.
Around 300 LNG ships are operational or on order. Large volumes of the gas are available but there is still a lack of infrastructure and bunkering facilities. Of the new vessels, 20% are cargo ships with slow-speed, two-stroke LNG engines [28].

Methanol

Methanol is safe, cost-effective and available due to existing global infrastructure. Currently methanol is available in 88 of the world's top 100 ports and with minor modifications in handling methanol bunkering is very straight forwards. The fuel reduces emissions of SO_x (-99%), NO_x(-80%), PM (-95%) and CO_2 (-13%) significantly. Methanol can be stored in standard fuel tanks for liquid fuel with minor modifications for the low-flashpoint properties. Methanol can be used in a two-stroke diesel cycle engine or four-stroke lean-burn Otto-cycle engines. The first engine to be able to burn methanol is the MAN BW ME-LGI 2-stroke dual fuel engine that can run on methanol, fuel oil, marine diesel oil or gas oil. At the moment eleven vessels are sailing on methanol with this engine [12]. The refit from diesel to dual-fuel methanol/diesel fuel costs around

250-350 € per kW for large, 10-25 mW engines. Methanol is also usable in fuel cells [28].
The cost of refit to use methanol is estimated to be less than other alternative fuels. There is no need for expensive exhaust gas after-treatment such as Selective Catalytic Reduction (SCR) and only minor modifications in storage facilities. IMO is still developing requirements for methanol within the *International code of safety for ships using gases or other low-flashpoint fuel*, the IGF code [28][59].

Biofuels

Biofuels are flexible and can blend easily with conventional fuel or be used as drop-in fuels (directly used in existing installations without significant technical modifications) to substitute conventional fuel. The most promising options are biodiesel and liquefied biogas (LBG), which consists primarily of methane. Biodiesel is most suitable to replace marine diesel oil (MDO) and marine gas oil (MGO). LBG is more suitable to replace LNG. Another option is hydro treated vegetable oil (HVO), which is most commonly used in ferries in Norway. HVO is available on a commercial scale and has a great GHG reduction when using waste oils and fats. HVO is therefore the most attractive short term option to de-carbonise shipping [27]. However, the International Energy Agency has determined the limitations of global biodiesel production based on oil crops and animal fats. Biodiesel is also in competition with other sectors such as aviation and road transport. To be able to meet demand, biofuels should also be made of lignocellulosic feedstock (plant dry matter). This increases the availability for shipping. Also dual-fuel with ethanol and biofuel increases the potential of biofuel [28].

Hydrogen and e-fuels

Hydrogen (H_2) can be produced by electricity from renewable sources, natural gas with CCS or nuclear energy. In the medium term hydrogen can be used in compressed or liquid form in fuel cells for short-sea shipping. Barriers that are still present are the high investment costs, the infancy of hydrogen as a fuel, the availability and price, the onboard storage space that is required and potential safety and approval requirements. The biggest barrier in using hydrogen is the low volumetric energy density of 8.5 GJ/m^3 for liquid hydrogen and 7.5 GJ/m^3 for compressed hydrogen. Hydrogen needs to be stored either at -253 ºC or under 700 bar pressure.
Hydrogen is also often the basis of electro-fuels, also known as e-fuels. This includes synthetic fuels, such as diesel, methane and methanol when produced from H_2 and CO_2, or from H_2 and nitrogen (N_2), such as ammonia. Both biofuels and carbon-based electro-fuels are drop-in fuels and require only limited or no modification to engines and fuel systems to replace or use in blend with traditional fuel in an internal combustion engine. The carbon-based fuels also have a high energy density. Nitrogen-based electro-fuels however (such as ammonia) require some modifications to engine, fuel storage and supply system in comparison to traditional fuels. The e-fuels are therefore an excellent bridging option during times of energy transition. Synthetic fuel needs similar onboard storage as conventional fuels. Electro-fuels have clear advantages such as technical application and GHG emission reduction. However, the production is currently quite expensive and energy intensive. The energy efficiency factor is not as high as when using direct supply of electricity for powering battery ships nor as efficient as of hydrogen. 73% of the electricity produced is available as energy for use in transport with direct supply. While using hydrogen in fuel cells is only 22% energy efficient and e-fuel only has a 13% efficiency. This impacts on the cost of fuel. Only if the electricity costs are low, the greater efficiency losses with e-fuels become less relevant [28].

Ammonia

Ammonia is a colourless gas which has a strong odour and is produced in large quantities all over the world. Ammonia (NH_3) is produced from nitrogen (N_2) mixed with hydrogen (H_2) gas and under the appropriate pressure and temperature. Green ammonia is produced with hydrogen from sustainable sources such as biomass, renewable electricity, nuclear and solar energy. Blue ammonia is produced with hydrocarbon and carbon capturing [3]. When oxidising ammonia, water and nitrogen is produced. By oxidising hydrogen only water is produced [77]. This raises the question why not hydrogen is used instead of ammonia. One of the reasons is that fuels with a nitrogen connection, such as ammonia, are easier to store and to transport and therefore are more economical in operation [77]. Secondly, hydrogen has a lower energy density and a very lower condensation temperature. Ammonia is liquid at -33.4°C and hydrogen only at -253°C [78]. It is also cheaper to produce a fuel cell for ammonia than hydrogen. This makes it the lowest source to tank ratio [77].
To be able to use ammonia as a fuel, modification of the engine, fuel storage and supply systems are needed. There are some issues that arise with the storage and handling of ammonia. First, the energy density of ammonia is half of the energy density of HFO. Together with the lower temperature and storage requirements,

this makes that the storage tanks triple in size for the same amount of energy [33]. Secondly, the use of ammonia comes with additional risks. Ammonia is a highly toxic substance for humans and the environment. Ammonia is lethal to humans at 2,700 ppm after an exposure of 10 minutes. Ammonia is also a flammable gas which is more difficult to ignite compared to conventional fuels. When using ammonia as a fuel, hydrogen is used for ignition. The flammability risk lies at 15%, which is 150,000 ppm. The flammability risk is therefore lower than the toxicity risk, but still significant.
In the potential of ammonia should be taken into account that the shipping market is competitive and any changes must be cost-effective. Ammonia is quite expensive, almost twice as much as HFO [5]. In 2019 a ton of ammonia amounted to 850 euro and a ton low sulphur 0.5% HFO only about 500 euro[24]. This can change in the future if the cost to produce ammonia diminishes. However, among the group of alternative fuels ammonia has the lowest cost per equivalent gallon of gasoline [79].
Besides the cost of fuel the Capex of the whole installation should be researched. Research has shown that the ammonia power configuration is 3.2 times more expensive as the conventional option [24]. The cost of an ICE electric version is approximately 2.9 million euro and that of a diesel-direct option is about 0.8 million euro. The cost of a fuel cell option for ammonia is approximately 2.5 million euro [42].

Batteries

Although technically speaking batteries are no fuels, they are yet discussed as a power source. Electricity from renewables or zero-carbon sources like nuclear energy, and in a maritime battery application is the only other commercially available options for carbon-free shipping. However, the batteries can only be used for short trades up to one hour and so for very small ships. For deep sea shipping batteries do not provide enough energy [28].

Comparing alternative fuel options

Figure 2.5 gives an overview of five of the alternative energy options and how they relate to each other. The fuels HVO and LNG score high on most fronts and the technical maturity is very high. The technical maturity of ammonia is rather low and the fuel availability, infrastructure, cost and rules are serious barriers on the path of implementation. Ammonia does however score higher on the capital expenditure and volumetric energy density than hydrogen, giving it a great advantage. With the barriers overcome, ammonia could be a very viable fuel for the future.

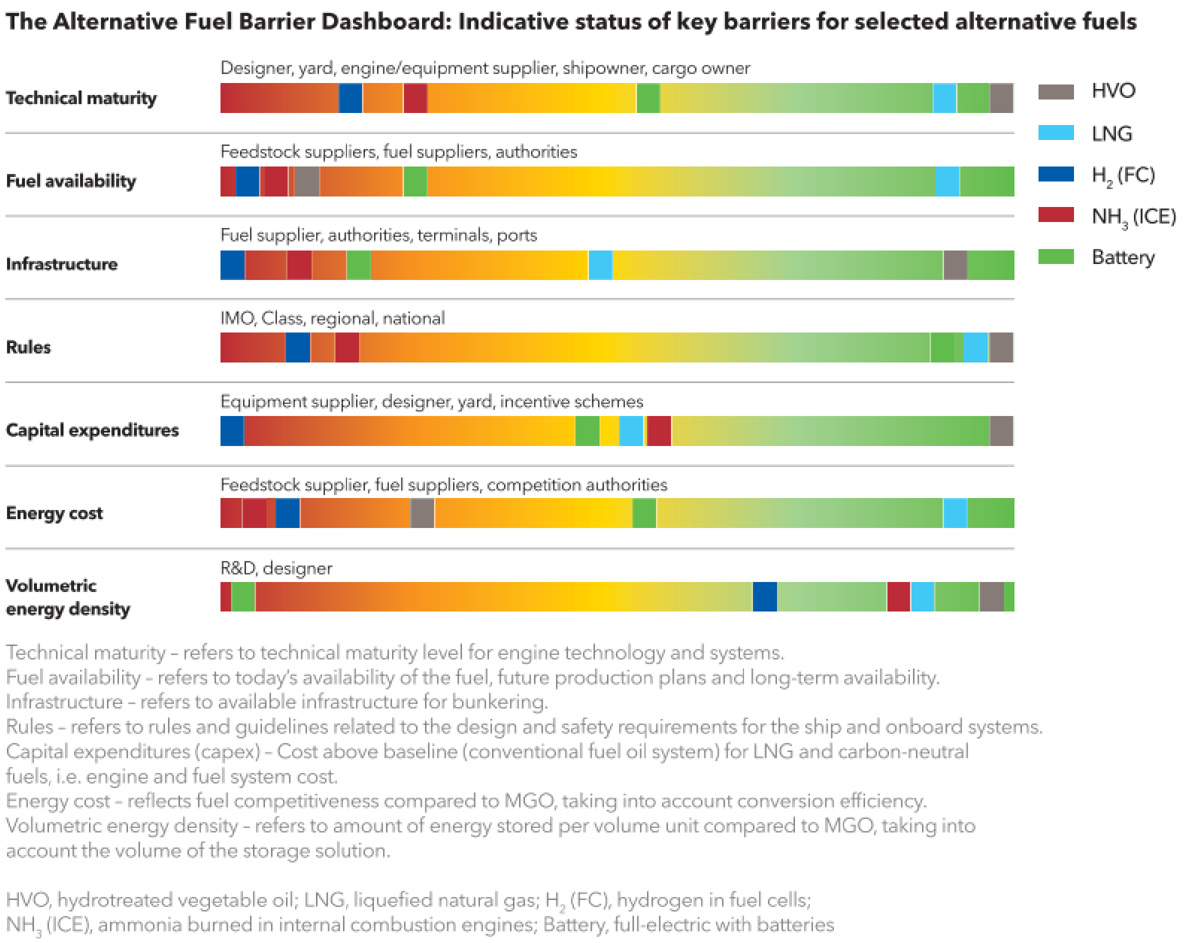

Figure 2.5: Fuel barrier dashboard [28]

The next table compares the alternative fuels in terms of energy density, volumetric energy density, renewable synthetic production cost, storage pressure and storage temperature. Here becomes clear what the advantages are of ammonia over hydrogen and ammonia is named as a balanced fuel.

Fuel type:	Energy density LHV [MJ/kg]	Volumetric energy density LHV [GJ/m3]	Renewable synthetic production cost [MJ/MJ]	Storage pressure [bar]	Storage temperature [°C]
Marine Gas Oil (reference)	42.8	36.6	Not applicable	1	20
Liquid Methane	50.0	23.4	2.3	1	-162
Ethanol	26.7	21.1	3.6	1	20
Methanol	19.9	15.8	2.6	1	20
Liquid Ammonia	18.6	12.7	1.8	1 or 10	-34 or 20
Liquid Hydrogen	120.0	8.5	1.8	1	-253
Compressed Hydrogen	120.0	7.5	1.7	700	20

Figure 2.6: Comparing ammonia to other renewable fuels [24]

Storage capacity

Storage capacity is an issue for many alternative fuels. Figure 2.7 depicts the volumetric energy density of fuel options and the gravimetric energy density (energy capacity per unit weight). For some fuels are the energy densities for the fuel-only and the storage system included option given. As can be seen is the option with the storage system included lower in both energy densities, due to the weight and volume of the storage solution. Especially for fuel in the gas phase high-pressure equipment is needed for compression and heavy chillers for cooling down. Ammonia has a low gravimetric energy density, which means less energy per unit weight. However volumetric energy density is more important when calculating the storage space needed. It is clear that diesel oils, bio and synthetic oils, together with gasoline still have the highest volumetric energy density. Ammonia, including the storage system is however better positioned than hydrogen. Not only has it better storage requirements (-34 °C instead of -252.85 °C or under 20 bar instead of 700 bar), it has also more energy per unit volume.

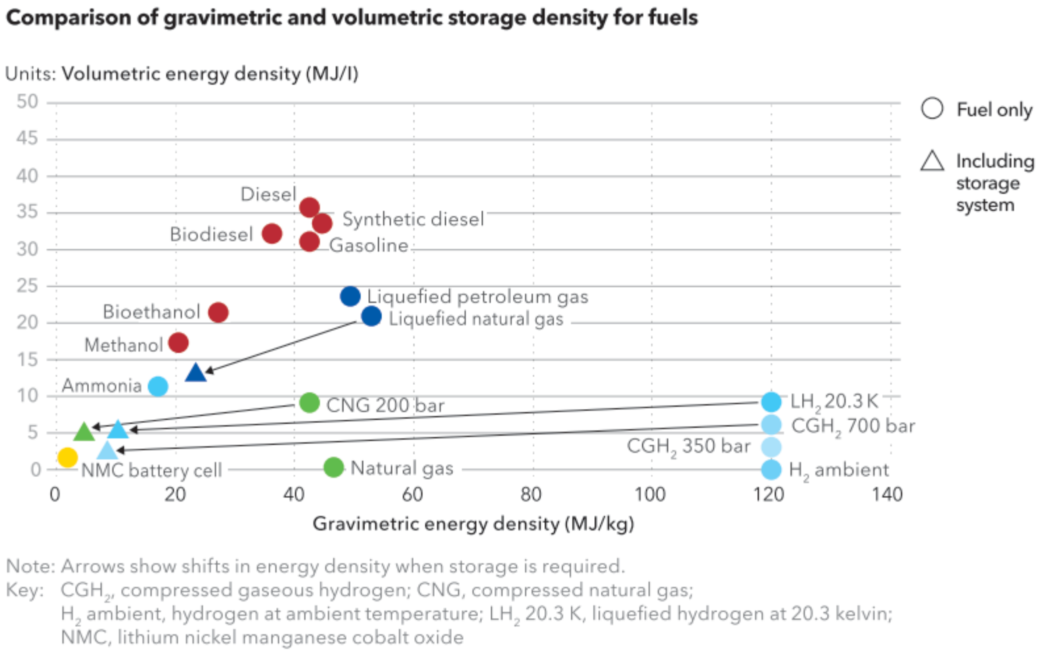

Figure 2.7: Comparison of gravimetric and volumetric storage density of fuels [28]

Fuels that are liquid at ambient temperature and atmospheric pressure are easier to store since the storage tanks can be easily integrated into the vessel's structure. This saves costs, weight and space compared to gaseous fuels. Ammonia requires tanks that are self-contained and non-integrated in the vessel's structure and that are heavily insulated. When changing the deep sea fleet to zero-carbon fuels alternative storage systems are needed. Also vessels probably must bunker more often. Figure 2.8 shows the bunkering intervals for alternative fuel options. It is clear that when using hydrogen, compressed and liquefied, deep sea sailing is not an option. The bunkering interval is only hours or days, so the vessel won't be able to make a full trip. Ammonia has an interval of weeks or months. Chapter 6 will elaborate on the fuel demand of the marine sector.

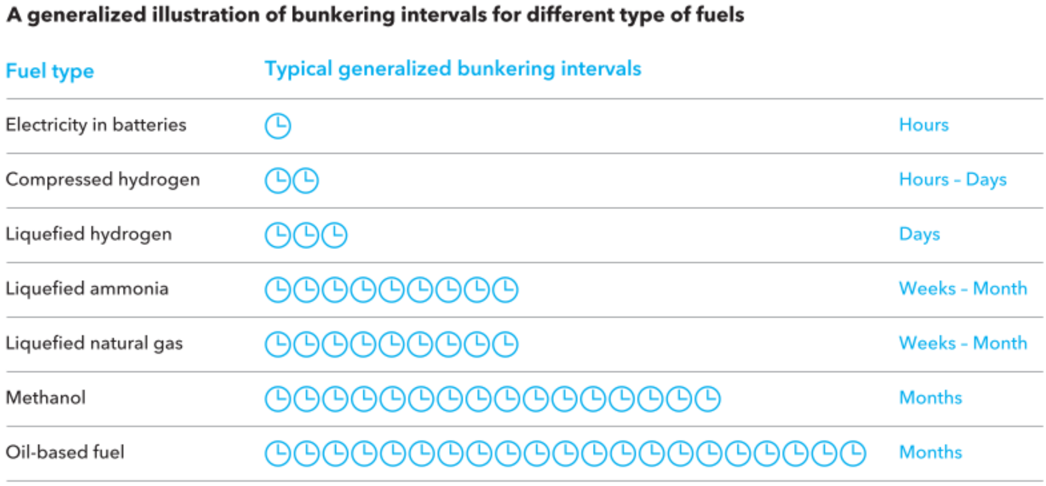

Figure 2.8: Bunkering intervals of alternative fuel options [28]

Future outlook

The future application of alternative fuels will depend on advantages and disadvantages for specific ships and ship sectors. In some sectors the fuel costs outweigh the capital expenditure, for other sectors on-board storage space requirements are more important. In the current world fleet in operation only 0.3% sails on alternative fuels with methanol (0.01%), LNG (0.14%) or battery (0.15%) as energy source. The vessels currently on order have a slightly larger share in green alternatives, hydrogen (0.04%), methanol (0.08%), LPG (0.13%), LNG (2,73%) and battery (3.07%). The other 93.95% in the order book for 2018 was all with conventional fuels [28].

DNV GL explored three possible routes for the world fleet to reduce CO_2 in which energy-efficiency measures, speed reduction and alternative fuels are simulated on basis of both existing and upcoming costs and policies. Two options focus on the path to meet the GHG emission reductions and the third option is the pathway to follow current policies. The pathways all predict a preferred use of liquefied methane (between 40 and 80% of the 2050 fuel mix). However, ammonia is the most promising carbon-neutral fuel option for new builds. This preference is due to lower cost of conversion, storage and the advantage of the fuel itself compared to H_2 and liquefied biogas (LBG)/synthetic methane. One of the routes is shown in figure 2.9. In this route regulations will require newbuilds from 2040 to be carbon-neutral. In all scenarios it is believed that the demand of seaborne trade will grow with 39% by 2050. The energy use per tonne-mile however is predicted to decline between 35 and 40% due to energy-efficiency measures such as hull and machinery improvements and speed reduction.

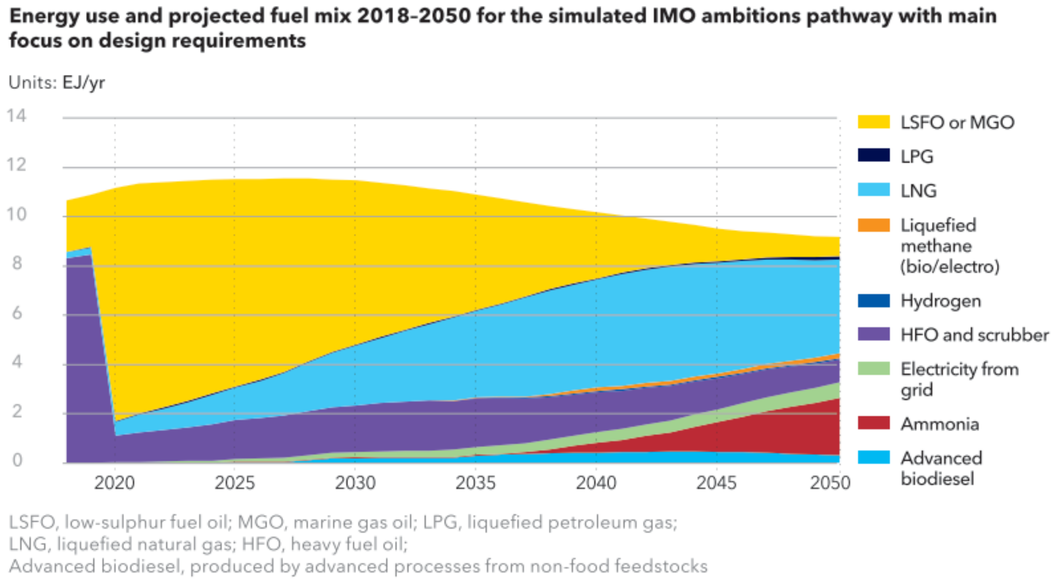

Figure 2.9: Pathway 1 with focus on design requirements [28]

The adoption of alternative fuels will take time as low-carbon fuels need to be developed, as well as production capacity and infrastructure. Ammonia is expected to become an important future marine fuel if a carbon-free production is developed, the necessary infrastructure is established and onboard converters are available. In the transition phase LPG could be used, since the fuel system can easily be converted to ammonia. It is believed that when looking into the future, fuel flexibility is key to meet de-carbonisation, as ship owners won't want to be locked onto a single option. This applies as well for issues such as storage, on-board tanks and port infrastructure. Ship owners need to make their vessels future proof for the changing and uncertain landscape to maintain competitiveness [28]. Chapter 5 will elaborate on this subject.

2.6. Ammonia

Ammonia has been labelled as a balanced fuel with barriers to overcome to be able to implement as an alternative fuel in the marine sector. While looking into the application of an alternative fuel in the marine sector, all aspects of that fuel should be researched. This section details and briefly discusses the aspects of ammonia.

Engine behaviour

There are two main configurations that are feasible for using ammonia. The options are internal combustion engine (ICE) and a fuel cell, or a combination of both. The fuel cell has a higher efficiency, but lacks power density, load response and is more expensive than the ICE. The ICE is therefore a more viable option.

Internal combustion engine

Research has shown that the most viable way to use ammonia as a fuel is in an internal combustion engine (ICE). In the engine first a catalyst is used to crack a small part of ammonia into nitrogen and hydrogen. Following the compression stroke hydrogen is used to ignite ammonia [33]. With the combustion only nitrogen and water are emitted [5]. An internal combustion engine has a high efficiency, is very practical and is of proven technology. An ICE is less expensive, more robust with acceptable power density and load response than solid oxide fuel cells (SOFC) [24]. Compared to an ICE with conventional fuel the ammonia ICE performs quite similar on power density, load response, part load performance and system efficiency [24].

Fuel cells

Another configuration to use ammonia is a solid oxide fuel cell (SOFC). Research shows that the fuel cell is the most efficient way to use ammonia. Fuel cells convert chemical energy through oxidation into electric energy

with a high efficiency and zero emissions. This pollution-free power source however, at this moment does not deliver enough power to drive ocean going vessels [5]. Fuel cells are already widely in use in submarines. In this application the ammonia is split fully and the hydrogen is used to generate electric energy [33].
One of the challenges when using ammonia in a fuel cell is that the conventional membrane, the proton exchange membrane that is used in hydrogen fuel cells, is not suitable [79]. This can be solved with the use of a hydroxide exchange membrane fuel cell (HEMFC). With this membrane the capacity of the fuel cell is increased to a maximum of 135 milliwatt per centimeter squared by working at a higher temperatures which accelerates ammonia oxidation. With this increase the fuel cell performs nearly as good as the fuel cell with hydrogen. The reason why ammonia fuel cells deliver less power is because ammonia oxidises more difficult than hydrogen [77].

Storage and handling of fuel

The easiest way to store ammonia is in liquid state which it will maintain at a temperature of -33.4°C [33]. There are some issues that arise with the storage and handling of ammonia. First, the energy density of ammonia is half of the energy density of HFO. Together with the lower temperature and storage requirements, this makes that the storage tanks triple in size for the same amount of energy [33]. Secondly, the use of ammonia comes with additional risks. Ammonia is a highly toxic substance for humans and the environment. Ammonia is lethal to humans at 2,700 ppm after an exposure of 10 minutes. Ammonia is also a flammable gas which is difficult to ignite compared to conventional fuels. When using ammonia as a fuel, hydrogen is used for ignition. The flammability risk lies at 15%, which is 150,000 ppm. The flammability risk is therefore lower than the toxicity risk, but still significant.
While storing and handling ammonia certain requirements must be met in order to reduce the risk and effect of exposure to society and environment. In order to safely handle and store ammonia, ammonia detection devices and ventilation need to be in place [24].

Application on-board

The use of ammonia on-board comes with a few issues. The storage of ammonia on-board requires larger tanks due to a lower energy density than conventional fuels. This will be either at the expense of the cargo space, which leads to reduced cost competitiveness, or impacts on the vessel's range. Infrastructure for short sea and in-land shipping should not be a problem, but deep sea shipping might currently not be an option when sailing on ammonia [27]. This is further discussed in chapter 6.
Another challenge in the use of ammonia is that it is probably not suitable for all ship types. Besides the split into inland and short sea shipping versus deep sea shipping, ammonia is only viable for constant load. Using ammonia in a DP-vessel could come with more challenges than it is beneficial. However, some research has looked into the application of an hybrid configuration with an electric engine to drive the propeller to deal with dynamic load and manoeuvring. More research is needed to show the potential in this aspect [42].
As mentioned before ammonia is toxic for people, animals and plants in large quantities[88]. To ensure that there is no contact between them is made, rules and regulations are put in place for production, storage and the use of ammonia. Modifications on-board to ship's equipment are needed to ensure the required safety level. These implementations can easily be made for purpose built vessels, but might be very challenging for a retrofit or other new designed ships. The application of on-board fuel cell systems specifically requires a new design of the electrical propulsion system and new storage capabilities compared to existing power plants [27]. These challenges will be later discussed in chapter 5.

Application infrastructure

Another aspect of the potential of ammonia lies in the necessary infrastructure. Prices of fossil fuels have been low lately which reduces competitiveness of non-fossil energy sources. It therefore delays the development of the infrastructure needed for alternative options [91]. Shipping companies prefer smooth port operations, accessibility and competitive pricing. Some ports, however, came up with some flexible solutions for the adaptation to new fuels such as ship to ship (STS) bunkering and temporary bunker stations. These stations can be used while infrastructure is being build [42]. Chapter 7 will elaborate on the subject of port logistics.

Production
Ammonia is a colourless gas which has a strong odour and is produced in large quantities all over the world. It is used for among other things fertiliser, detergent and coolant for cooling installations [88]. The method to produce ammonia is the Haber-Bosch process. In this process a flow of nitrogen (N_2) gas stream is mixed with hydrogen (H_2) gas and under the right pressure and temperature produces ammonia (NH_3). So-called green ammonia is produced when the hydrogen stems from sustainable sources such as biomass, renewable electricity, nuclear and solar energy. When the process is fuelled by hydrocarbons, the product is called blue ammonia [3]. The Institute for Sustainable Process Technology (ISPT) has started a project to form hydrogen by water electrolysis powered by solar and wind energy to produce green ammonia [33]. Chapter 8 will elaborate on the production process and location of the production plant.

Price and investment cost
In the potential of ammonia should be taken into account that the shipping market is competitive and any changes must be cost-effective. Ammonia is quite expensive, almost twice as much as HFO [5]. In 2019 a ton of ammonia amounted to 850 euro and a ton low sulphur 0.5% HFO only to about 500 euro[24]. This can change in the future if the cost to produce ammonia diminishes. However, among the group of alternative fuels ammonia has the lowest cost per equivalent gallon of gasoline [79].
Besides the cost for fuel the Capex of the whole installation should be researched. Research has shown that the ammonia power configuration is 3.2 times as expensive as the conventional option [24]. The cost of an ICE electric version is approximately 2.9 million euro and that of a diesel-direct option is about 0.8 million euro. The cost of a fuel cell option for ammonia is approximately 2.5 million euro [42].

Industry components
The following components all have an influence on the potential of ammonia as an alternative fuel.

- The supply chain of the fuel market. This includes production, distribution, storage and handling of the fuel
- Port infrastructure
- Infrastructure for long distance routing
- Engine performance. This includes the volumetric energy density and influence of ammonia on the engine (less power available, smaller ramp-up features).
- Feasible engine options and other components of the power plant
- Applicable ship types. This includes design and retrofit options
- The potential loss of cargo space
- The demand of fuel for the shipping sector
- Rules and regulations in terms of safety of society and environment
- Emission limits
- Design requirements and integration risk
- Marine industry as competitor to other sectors

2.7. Researched potential
This section discusses the research that has been done so far on the potential of ammonia, mostly compared to other fuels. A main division is between short term where research shows that ammonia has no potential ([35]) and long term research which says that ammonia is the future ([28], [34] & [9]). This section will elaborate on the research done leading towards the subject of this thesis.

Short term
Hansson et al. [35] looked into the prospect of ammonia as a marine fuel compared to other alternative fuels.

The approach of the research first is to develop a model of an energy system including cost-effectiveness of alternative fuels for researching global climate targets. Secondly a multi-criteria decision analysis (MCDA) is made to rank the fuel options on basis of performance and the criteria based on maritime stakeholder preference. This research came to the conclusion that hydrogen is a more cost-effective option than ammonia, but ammonia has as much potential in the MCDA and looking at the shipping related stakeholders. They state that ammonia is an interesting future marine fuel option, but many issues must be solved before a large scale introduction can be realised.
Alternative fuels should comply with issues as availability, cost, energy density, technical maturity and environmental impact. Looking into the last item, ammonia has a low climate impact if produced from either renewable energy and/or produced in combination with carbon capture and storage (CCS). Currently, ammonia is produced from fossil fuel-based hydrogen. However, the production process for renewable ammonia is under development [35]. This statement is supported with figure 2.5. The technology to implement alternative fuels already exists, but is not ready for large scale implementation.

Long term
When looking into the researches that focused on long term solution, there are a few predictions made. Halim et al. [34] assumes the market share of hydrogen and ammonia in 2035 to be 70%. Another research, Ben Brahim et al. [9], looked into climate-neutral shipping by 2050 for the Danish maritime cargo sector and names hydrogen, methanol and ammonia as the most preferable fuel from the socioeconomic cost perspective.
DNV GL [28] research resulted in a maritime forecast for 2050 as part of their Energy transition outlook series. This fits into the IMO GHG reduction strategy and the growing pressure on shipping to cut down on emission. DNV GL looked into the world fleet decarbonisation and the readiness level of alternative fuels to scale for wider demand. Deep-sea sailing is responsible for 80% of all CO_2 emissions of the global fleet. Short sea shipping, however, is already slowly changing towards low- or zero-carbon technologies, such as batteries and hydrogen fuel. The main clean options for deep sea sailing are LNG, which is not carbon neutral, and biofuels which are quite expensive and not widely available. DNV GL is convinced that in 2050 alternative and carbon neutral fuels are used alongside traditional fuels that are more established at the moment, such as LNG. Carbon-neutral refers to an energy source or system that has no GHG emissions or carbon footprint.

2.8. Conclusion

Concluding the research that has been done so far, a division can be made between broad and in-dept studies. The broad studies of Volger [87], Hansson et al. [35] and DNV GL [28] looked into most aspects, but are also based on a number of assumptions.
The study from Hansson et al. [35] looked into the short term implementation looking at cost, energy density, technical maturity and environmental impact. They used energy system modelling including cost-effectiveness and a multi-criteria decision analysis (MCDA) to rank fuel options on the basis of performance and preference of stakeholders. They stated that ammonia has potential but there are a number of barriers to overcome before large scale implementation. These barriers are not further researched.
DNV GL looked into the long term implementation of ammonia by looking into the potential of ammonia by comparing the fuel to other alternative fuel options on technical maturity, fuel availability, infrastructure, rules, capital expenditure, energy cost and volumetric energy density. They also looked into the storage capacity compared to other fuels. All these aspects are still based on assumptions that barrier, such as sufficient production capacity and infrastructure for the supply chain, onboard converters and storage and port infrastructure, will have been overcome by 2030. This research gives a good insight in the future of ammonia as a marine fuel, but there are still a number of assumptions made.
Another broad study is of Volger [87] who looked into the environmental impact of alternative fuels on cruise ships. He first looked into the alternative fuel options applicable for cruise ships, which also included ammonia. The came to the conclusion that hydrogen has the largest impact on ship design, followed by ammonia. The study analysed the environmental impact with a design tool that was build specific for cruise ships. The research looked into a number of aspects, namely storage on board (hydrogen needs to be stored at cryogenic conditions, requires a lot of storage), power conversion system (hydrogen and ammonia can be used in a fuel cell and methanol in both fuel cell and ICE) and cost considerations (with a cost prediction with operating ex-

penditure (OPEX) and capital expenditure (CAPEX)). This study however does not consider the supply chain with port operations and production plants.

Detailed studies, for example De Vries [24] that researched potential engines for sailing on ammonia, looked into smaller aspects. These studies have not looked into the correlation between the aspects. This thesis will make an integral model of all aspect and how they influence each other. This will be done with the research questions named in the next chapter.

3
Problem definition

The previous chapter provided some background information on why alternative fuels should be implemented and the choices available. As discussed ammonia is at the moment not a very strong option, but studies show that it could become a strong option in the future and should therefore be studied more in depth.

Main research question

Previous studies often focus on one part of the well to wake chain and use assumptions on the implementation of ammonia. This thesis looks into the path of implementation of ammonia in the marine industry, including all aspects and how these aspects influence each other. This is done by looking into the barriers on the way of implementation and whether these barriers can be overcome by 2030. This year has been named as the moment that barriers of implementing ammonia should be overcome [28]. The main research question is therefore the following:

What are the critical success factors of ammonia to fuel the marine industry by 2030?

Critical success factors are indications for opportunities, activities or conditions required to achieve an objective. These variables have an impact in whether the objective is successful and effective, and need to be enabled for a positive outcome [83]. In other words, these are the barriers currently in the way of implementing ammonia in the marine industry.

Sub research questions

In order to determine the critical success factors, first the operational profile and the power plant installation for which ammonia is applicable is determined. This also includes the power plant set up and the design features. This sub question will provide the marine sub sectors for which it is viable to sail on ammonia.

For which operational profiles and power plant installations is ammonia applicable?

Chapter 5 discusses first the optional power plant configurations for the use of ammonia. The barrier of using ammonia as a fuel in a power plant is the availability of an engine that can run on ammonia. Next the impact on design of switching to ammonia will be discussed. The storage and providing of fuel to the engine is more complex and takes up more space than the system of conventional fuel options. This has therefore impact on the the design of the vessel. The final barrier is the regulations for sailing, storing and using a toxic substance as a fuel in the IGF code. The rules are not yet in place for ammonia.

When the critical success factors and their timeline of the operational and design side of the vessel are determined, the routing of the vessels in the scope is researched with the following sub question.

To what extent does the shipping range of ammonia coincide with the current trading corridors?

As mentioned in section 2.6, ammonia has a larger storage space than conventional fuels. In the case of HFO it triples in size. This will lead to either loss of cargo space or a shorter distance travelled. For the most common routes sailed of the vessels in the scope the energy demand is calculated and analysed to see if the vessels are still able to complete the route.
Researches have looked into the possibilities of other alternative fuels in the marine sector and the impact on routing, but not yet for ammonia [28][87][47]. The methods used however can also be used to determine the routes and energy demand. The barrier in this section is the lower energy density of ammonia in comparison to conventional fuel. This requires larger fuel tank which could lead to an extra stop or substitute cargo. An extra stop can cause changes in the logistic chain.

Along the current shipping corridor are the most used ports located. Out of the main 400 major bunker ports just six ports are supplying 60% of the world's demand [13]. These ports are located very strategically. For vessels to switch to ammonia, the fuel needs to be available in these ports. This is discussed with the next sub question.

To what extent are important ports able to provide ammonia bunkering facilities?

The barrier in this part of the supply chain is the storage abilities in the ports. This includes infrastructure and storage itself as well as investment costs. Another barrier in this section is uncertainties in regard to policies in specific ports.

The final step in the chain is the production. For this aspect it is important to research location and process.

To what extent are the production locations able to supply current and future fuel demand?

First, the production process is described and the current availability of ammonia and locations of the production plant. While looking into the production process a few factors are important. First, the emissions of the production process itself. It is desirable to produce green ammonia instead of blue ammonia to reduce or minimise emissions. Green ammonia production requires renewable energy. While looking into a location, renewable energy sources should be available nearby. The second factor is fuel demand and the capacity of the production plants. It is important to keep competition with other sectors in mind. If the demand is significantly larger than the supply, the price of ammonia will likely increase, which makes the implementation of ammonia less likely.
Then an assumption has to be made of the share of ammonia in the marine fuel mix in 2030 to calculate the future production. Also the fuel costs and investment cost are discussed.
The first barrier in this section is the production capacity of green ammonia and investment costs required to produce green ammonia. The second barrier is the price of green ammonia, which is higher than conventional fuel. This also includes potential competition with other sectors, which could drive up the price.

4
Methodology

Chapter 3 discusses the research questions and a short overview of how this thesis will discuss and analyse the critical success factors of all the aspect in the marine industry. This chapter discusses first the gap in research and what this thesis adds to the research of ammonia, followed by the scope. Then an overview of all the barriers is given and how these barriers influence all the stakeholders involved. Finally, the model of how the critical success factors are calculated in the following chapters is discussed.

4.1. Gap in research

The research into potential can be divided into looking into short term and long term feasibility, mostly compared to other fuels. A study from Hansson et al. [35] that looked into the short term implementation looked at cost, energy density, technical maturity and environmental impact. They used energy system modelling including cost-effectiveness and a multi-criteria decision analysis (MCDA) to rank fuel options on the basis of performance and preference of stakeholders. They stated that ammonia has potential but there are a number of barriers to overcome before large scale implementation.

Looking into long term implementation one study stands out, namely that of DNV GL [28]. They are convinced that ammonia will have a large role in the future. They looked into the potential of ammonia by comparing the fuel to other alternative fuel options on technical maturity, fuel availability, infrastructure, rules, capital expenditure, energy cost and volumetric energy density. They also looked into the storage capacity compared to other fuels. All these aspects are still based on assumptions that barriers, such as sufficient production capacity and infrastructure for the supply chain, onboard converters and storage and port infrastructure, will have been overcome by 2030. This research gives a good insight in the future of ammonia as a marine fuel, but there are still a number of assumptions made. These assumptions are aspects that needs to be integrated in their model.

Both the short and long term researches focused mainly on comparing ammonia to other alternative fuels on certain aspects. There is however little research that combines all aspects of ammonia into one model. This thesis focuses on all aspects of ammonia and the interaction between the aspects while looking into the critical path of implementation and which barriers need to be overcome. This will be done by a step-by-step approach. First the operational profile is researched for which segments of the marine sector ammonia has the highest probability of being a potential and feasible fuel. This also includes the power system, design criteria and regulations for using ammonia on board. Then the most common routes of vessels in these segments are discussed, including energy demand. This entails the distance a vessel can sail on ammonia, which has a lower energy density than conventional fuels. The next step is the production process and the capacity and costs involved. The barriers per aspect involved and the relation between these barriers are discussed in section 4.3.

4.2. Scope

This thesis is an integral research on all the aspects involved in determining the potential of ammonia. Since all the aspect are correlated, they all fall within the scope. However, this thesis will mainly focus on the deep

sea sailing sector and not so much on the inland and short sea shipping sector. This thesis focuses only on ammonia. Comparisons to other alternative fuels are made in some regard, but no further research in other alternative fuels is done.
All aspects are discussed with a literature study to get a broad understanding of the subject. This thesis will however not go into too much depth on all aspects. The in-depth research is either already done and is named in the literature study, or can be researched further on.

4.3. Barriers

The driver for the marine sector to switch to an alternative fuel is the concern about the environment and the Paris Agreement to strive for a cleaner world. The IMO has the task to stimulate demand for alternative fuel over conventional fuel to reach the set goals of the Paris Agreement. This is done by implementing rules and legislation to which the ship owners needs to comply. The ship owners are influenced by these rules and legislation to switch to a cleaner fuel option. The ship owner has a number of options to switch to and will only switch to an option when the following aspects, shown in figure 4.1, comply with the fuel characteristics. Per aspect the barriers are listed and further discussed below. The aspects that needs to comply to the alternative fuels are the engine, the fuel itself, port logistics, price, operations, vessel lay-out and legislation and rules. The various aspects and the mutual relationship are depicted in the next diagram.

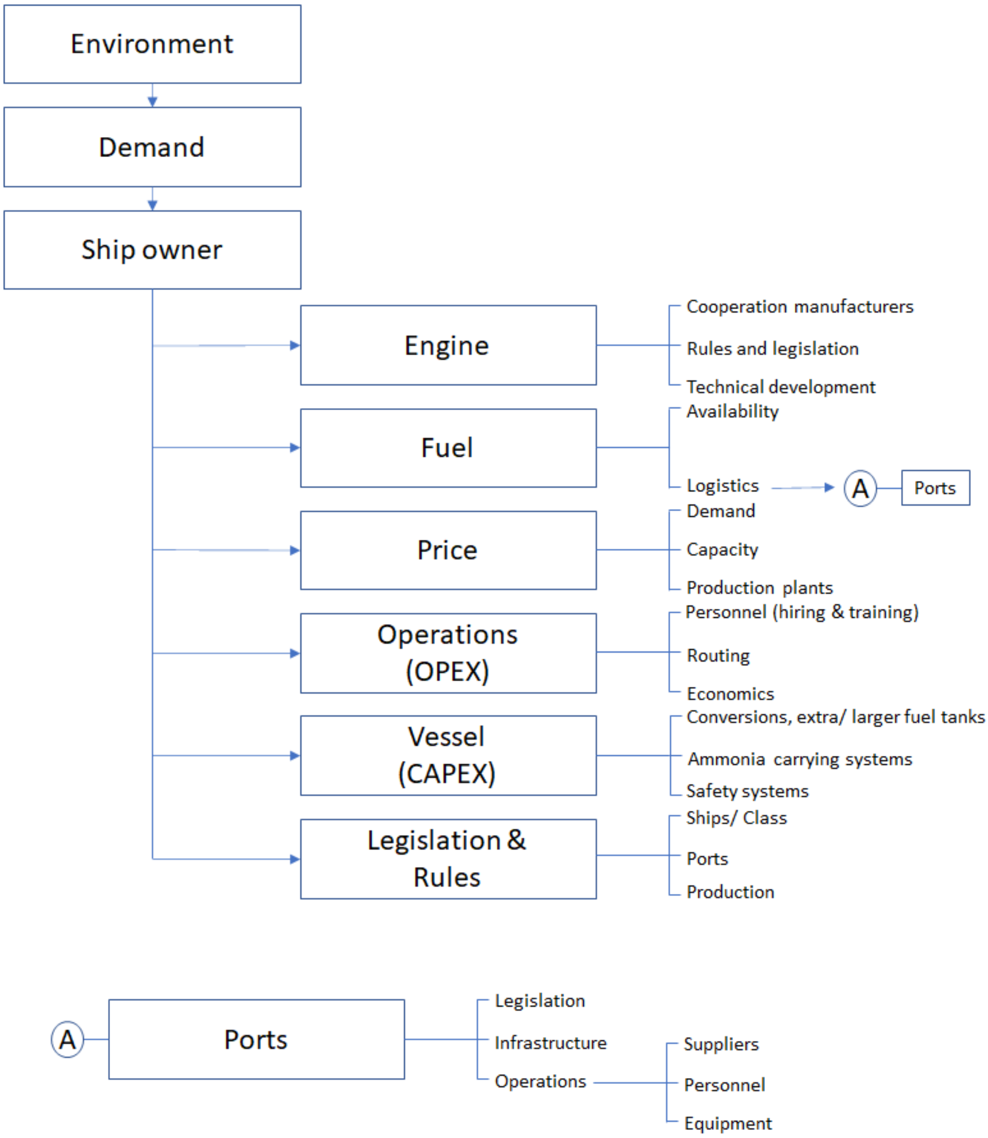

Figure 4.1: Model with all aspects and their mutual interaction and relationship

Engine
For the ship owner to switch to an alternative fuel, an engine that can run on ammonia needs to be available. This requires cooperation of the manufacturers to manufacture such an engine that can run on ammonia. This engine needs to comply with a number of rules and legislation regarding technical requirements set by the IMO. The third barrier is the technical development of the engine itself. This entails the technical readiness level of the technology for engines to be able to run on ammonia.

Fuel
The second aspect, the fuel, has the barriers that it needs to be available for the ship owner, both in volume and location. This entails production capacity for grey, blue and green ammonia to ensure enough ammonia is available. The logistics of supplying the fuel from production plant to the ship also entails port logistics.

Port
The logistics of getting the fuel from the production plant to the vessel are summarised in this aspect under operations. The first barrier in this element lies for the supplier of the fuel, in the hiring and training of personnel and the equipment needed to transport the fuel. The second barrier lies port side in the legislation and the uncertainties in port policies. The third barrier is the infrastructure of the port to be able to store and handle ammonia.

Price
The price of ammonia is based on the demand and availability of the fuel. The current demand of ammonia is for 80% for the use of fertilisers. If the marine sector increases the demand for ammonia, the price will likely rise, making the switch to ammonia less desirable. The capacity of ammonia production is a large barrier for implementing ammonia.

Operations (OPEX)
The operations of the vessel entail personnel, routing and the overall economics. Personnel needs to be hired and trained for safely handling ammonia. The routing is impacted by the switch to ammonia due to the lower energy density of ammonia compared to conventional fuel options. For the same energy output, a greater volume of fuel is needed. This requires either extra stop overs during the voyage or a larger fuel tanks which could lead to loss of cargo space. The final barrier is the economics. The price of alternative fuels will always be higher than conventional fuel. Ship owners will look at the most profitable fuel option when switching to an alternative fuel. This is also strongly related to the next aspect.

Vessel (CAPEX)
The vessels currently sailing or on order, are not equipped to sail on ammonia. The main issue is the lower energy density of ammonia, which required extra or larger fuel tanks for the same energy output. Also, storing of and supplying ammonia to the engine and bunkering of ammonia, requires different systems since it is a toxic substance. Finally, a number of safety system are required. Vessels need to be refitted to be able to sail on ammonia. This greatly influences the Capital Expenditure, which is a very important decision factor on the ship owners decision.

Legislation and rules
The final aspect is the legislation and rules that are applicable for alternative fuel specifically. The rules are divided in three categories, viz. ships, ports and production. The ships need to comply with the class from a Classification Society. The ports and production plant need to comply with legislation about safely and environmental friendly operating.

Dependency table

The dependency table 4.1 shows the relation between the barrier categories and the influence on another. The sign indicates the influence that aspects in the first column have on the aspects in columns two through eight. The sign ++ means a strong influence, + a moderate influence, +/- a small influence and - for no influence. The diagonal has no values since since an aspect does not impact on itself.

	Engine	Legislation (incl. Class)	Demand	Price fuel	Production	Port infrastructure	Design
Engine	X	+	++	-	+/-	-	+
Legislation (incl. Class)	+	X	+	+	+	+	++
Demand	+	+/-	X	++	++	++	-
Price fuel	-	-	++	X	+	-	-
Production	+/-	-	+	++	X	+	-
Port infrastructure	-	+/-	+/-	-	+/-	X	+
Design	-	++	+/-	-	-	+	X

Table 4.1: Interdependency matrix of the barriers

Engine availability
The engine availability has a moderate influence on legislation, since if the manufacturers are building an engine, the IMO needs to finalise the rules about the technical requirements to which the engine needs to comply.
The engine availability does have a strong influence on the demand for ammonia. As long as there is no engine that runs on ammonia, the demand for ammonia from the marine industry stays low. Only with an engine available, the demand for ammonia can rise.
The availability of the engine has no direct influence on the price of the fuel or port infrastructure, only through demand.
The influence on production is small since it does not directly influence the production numbers, but can promote investment for production plant investments.
Finally, there is a moderate influence on the design of the vessel. The engine has different technical requirements when running of ammonia than conventional fuels, but the major influence will come from the legislation.

Legislation
The influence of legislation is for all aspect moderate, except for the design requirements. The legislation requires safety systems and specific design requirements to be able to safely handle ammonia as a fuel, which have a large impact on the design of the vessel. Vessels that are already operable and of which the owners consider to switch to another fuel need to refit to comply with the rules. For the other aspects, the legislation coming into effect has an supportive influence since it lowers the risk of switching to ammonia. With the rules in place, manufactures are stimulated to develop an engine that can run on ammonia, the demand for the fuel rises, the production and investment in production plants as well as the port infrastructure are stimulated.

Demand
Currently the demand for ammonia is low, since there are no engines available yet that are able to use ammonia as a fuel. Designing an engine for a fuel that is not yet available is a very high risk if implementation of regulations is delayed and the demand stays low.
The demand for ammonia has a strong influence of most aspects, except for engine availability, legislation and design. For the engine availability the demand is classified as moderate, since the engine itself will not change significantly if the demand rises. An initial demand has a positive influence of the availability of the engine, but after a certain number, the engines are manufactured in spite of further rise of the demand.
The demand has a low influence on the legislation. The IMO is mostly stimulated by the Paris Agreement, which is requiring cleaner fuel options to be implemented in the marine sector. An initial demand for ammonia can stimulate the process of implementing ammonia in the rules, but once the rules are finalised, a greater demand will not influence the rules.
Another aspect greatly impacted by demand is production. Currently, there are multiple production locations for ammonia since it is globally used as a fertiliser. The ammonia produced is all brown or blue ammonia, while no green ammonia production is available yet. Investments are needed to convert production plants to produce green or hybrid ammonia. It is however, unlikely that stakeholders will invest in green ammonia production when the demand is still low. The current production capacity is also not at the level to fuel a

significant part of the global fleet, now or by 2030. Scaling up to meet this level also requires investments.
Scaling up is also an important aspect of the fuel price. If a part of the marine sector switches to ammonia and the capacity is not increased, the fuel price will likely rise, whereas the marine sector is also in competition with other sectors. This will then again influence the fuel demand.
Finally, the demand has a great influence on the port infrastructure. Ports need to be able to process the rising volume of ammonia with suitable storage and bunkering to the vessel.

Price fuel
The fuel price does not have any direct influence on the engine availability, legislation, port infrastructure or design of the vessel. The price of the fuel does not impact the way of storing, handling or running on ammonia. The price does have a strong influence of demand. If the price rises, the demand is likely to decrease.
The prise of the fuel has an influence on the production as well. With a higher prices, investing in production plants becomes more attractive, but the production itself might stay the same. This is more influenced by the demand of the fuel.

Production
The production of ammonia has a low influence on the engine availability. An initial production of ammonia for the marine sector can stimulate the development of an engine, but just as with demand, the engines are produced at a certain number in spite of further growth in production of ammonia.
Legislation of the use of ammonia is not influenced by production levels and neither is the design of the vessel.
The production levels have a moderate influence on the demand of ammonia. If there is an initial demand and the production is increased, the demand increases as well, since there is more fuel available. If the demand remains low, the increased production will not change this. Demand is a greater influence on the production than the other way around.
Production does have a great influence on the fuel price. If the production levels are lower than the demand, the fuel price will be higher than when supply does meet demand. The greater the production volume, the lower the price, until an optimum is reached. This also entails the need for investment in production plants. With a greater volume produced, the price will decrease. This also has an influence of the port infrastructure. With a higher produced volume, more ammonia storage and handling facilities are needed in the port infrastructure.

Port infrastructure
The port facilities have no influence on the engine availability and fuel price. It does have an moderate influence on the design of the vessel, since bunkering ammonia is different than conventional fuels. The design of the vessel needs to be able to handle this process.
The port infrastructure has a small influence on the legislation since the port authorities can stimulate the IMO to implement ammonia in the rules to make clear to what rules the ports need to comply with. This is however a small influence and the relation the other way around has a larger influence.
The influence on the demand and the production is also small. For initial demand and production the storage facilities in the port are of influence, since it lowers the risk of sailing to a port with no bunkering possibilities available. This lowers the risk of switching to ammonia. However, the port infrastructure is more influenced by the demand and production than the other way around.

Design of the vessel
The design of the vessel has no influence on the engine availability, fuel price or production. The design requirements do have a large influence on the legislation. The IMO needs to determine if the vessels currently sailing are suitable to switch to ammonia, and if not, what the requirements are to do so.
The design of the vessel has a small influence on the demand. If the requirements are too strict to realise, demand will decrease.
The influence of vessel design on the port infrastructure are moderate. The bunkering and storing of ammonia is different than conventional fuel, so vessel design influences the process of bunkering for the port side.

4.4. Model

The previous section describes the critical success factors and the influence they have on each other and the aspect of the marine industry. This section describes the model that will be used to calculate the needed indicators. As mentioned the lower energy density of ammonia is a significant barrier for the implementation of ammonia as fuel for ocean going vessels, which are the vessels in the scope. The first step is determining the operational profile of the vessels in the scope.

4.4.1. Routing

There are some options to determine the routes that commercial vessels use and the energy demand along these sailing routes. Below three methods are discussed and whether these can be used for this research. The third method is discussed in more detail.

Master

For the research of DNV GL the software MASTER has been used to map the world fleet's CO_2 emissions. This model uses global ship tracking data from AIS added with ship specific data. Recording ship traffic is mandatory for ships larger than 300 gt that sail internationally and for all cargo ships greater than 500 gt. AIS has recorded the traffic of approximately 86,000 vessels in 2018. AIS also tracked a large number of small fishing vessels and other small ships that don't have a trackers [28]. There are some sites to gather information from AIS trackers, but to obtain raw data to analyse is difficult and this method is therefore not further used in this research. Another study (Volger [87]) has also used AIS data to analyse data. This study used the data to predict ship's speed over different types of operations. This particular variable is not needed in this research.

Clarkson and Fearnleys

The Third IMO GHG study researched the emission projection with predicted transport demand, global economic growth (GDP) and energy consumption in 2050. Historical data from Fearnleys was used and complemented with data from Clarkson in combination with external drivers of transport growth, such as economic development. Clarkson has a better distinction between vessel and cargo type and more comprehensive coverage. Fearnleys however goes further back in time with data. There is a causative relation between the GDP and the volume of shipping transport, viz. R^2 = 0.98 [45]. As mentioned in chapter 2 is it believed that the volume of seaborne trade will grow with 39% by 2050. The energy use per tonne-mile is believed to decline between 35 and 40% due to energy-efficiency measures such as hull and machinery improvements and speed reduction [28]. This needs to be taken into account with this method. This model is not further used since the application of ammonia is different than conventional fuels.

SAVE model

Research looked into the possibility of the replacement of fossil fuel by hydrogen in the route between China and the United States. This is the busiest container shipping lane in the world. In 2015 24 million TEU was moved across the Pacific, which is 46% of the world total.

The research looked into energy demand and refuelling needs for a fleet of container ships between China and the USA in order to establish the feasibility of powering ships with hydrogen fuel cells. Currently there is no infrastructure along the route, so the research also identified ports where hydrogen should be available.

First the baseline energy demand is determined for container ships between the busiest ports of the route, namely Pearl River Delta (PRD) in China and San Pedro Bay (SPB) in the USA. After the fuel requirement is established, space requirement is also clear. The difference here is that hydrogen is stored as a cryogenic liquid (stored at extremely low temperature), where ammonia needs less space intense equipment [28].

After the space and fuel needed are clear, the number of voyages the container vessel can complete is calculated. To improve the attainment rate of the ship two options are reviewed, viz. sacrifice some cargo space or make an extra refuelling stop along the route. The research established that 99% of the voyages can be completed with hydrogen as fuel with only minor changes implemented, being replacing 5% of cargo space or adding one port stop. Without these measures 43% can be completed.

Mao et al. [47] used their Systematic Assessment of Vessel Emission (SAVE) model to calculate the amount of energy the ships used during the voyage and whether liquid hydrogen could be stored to meet the energy need. To asses whether the vessel can carry enough fuel the number of voyages the vessel can sail is calculated, where a voyage is identified as a trip between two ports. One voyage can consist of multiple trips if a stop at an extra port is made. the assessment is carried out as follows:

- Identify ships trading along the route, including the exact voyages completed and which ports are visited

- Estimate the basic energy demand for those voyages on fossil fuel
- Model the volume and liquid hydrogen fuel needed for the voyages. Compare the results with the space available for fuel
- Assess the attainment rate without replacing cargo or adding a stop when hydrogen is used
- Evaluate the two options, viz. replacing cargo space and refuel more frequently to improve attainment rate.

Mao et al. [47] used the data from the device Automatic identification system (AIS) and narrowed it down to the North Pacific Ocean in 2015. Then they used the ICCT's SAVE model to identify when ships were at berth to determine the vessel's port of origin for that leg. The amount of energy the container vessels needed is used as a baseline, obtained from the SAVE model. The SAVE model uses a bottom-up method for the estimate hourly energy demand for each individual ship. This energy demand per hour is known as $E_{required}$.
Then the volumetric energy demand is calculated by formula 4.1 in m^3.

$$V_{LH_2 need_l} = \frac{E_{required_l}}{D_{LH_2} \cdot \eta_{LH_2}} \cdot \text{fuel margin} \tag{4.1}$$

$V_{LH_2 need_l}$	Volumetric energy demand in m^3
$E_{required}$	Energy demand in kWh
D_{LH_2}	Volumetric density of fuel system, including the equipment for storage of hydrogen. The density of liquid hydrogen is adjusted from 71 to 40 kg/m^3. This compensates for the insulation tanks and other fuel system components. Multiplying with hydrogen's energy density of 33.3 kWh/kg gives 1,332 kWh/m^3
η_{LH_2}	The efficiency of hydrogen fuel cells is assumed to be 54%
Fuel margin	The extra fuel a ship carriers as a safety margin. This margin is 1.2 for all ships.

Table 4.2: Volumetric energy demand

The available space for liquid hydrogen fuel systems is calculated with the following formula.

$$V_{LH_2 capacity_l} = 5 \cdot V_{E_i} - 2 \cdot V_{FC_i} + V_{f_i} \tag{4.2}$$

$V_{LH_2 capacity_i}$	Available space for liquid hydrogen fuel system on board ship i in m^3
V_{e_i}	Volume taken up by existing engine on board ship i in m^3
V_{FC_i}	Volume of fuel cell system for same output power on ship i in m^3
V_{f_i}	Volume taken up by existing fuel tanks on ship i, m^3

Table 4.3: Volumetric space available

The volume of the existing machinery space with an internal combustion engine is estimated with the following rule of thumb.

$$V_{e_i} = \frac{P_{ME_i - 1906}}{54.066} \tag{4.3}$$

The volume needed for the hydrogen fuel cell is then calculated with:

$$V_{FC_i} = \frac{P_{ME_i} - 73.331}{55.944} \tag{4.4}$$

Substitute cargo

There are two options to improve attainment rate. The first one is sacrificing cargo space. One TEU has a volume of 38 m^3. The other option is more frequent bunkering. First the maximum range of each ship is calculated with the available space. This is done with the following equation.

$$R_i = v_{avg_i} \cdot \left(\frac{\left(\frac{V_{LH_2 capacity_i}}{\text{fuel margin}} \right) \cdot D_{LH_2} \cdot \eta_{LH_2}}{P_{ave_i}} \right) \tag{4.5}$$

R_i	Range of ship i, using space on board with fuel margin
P_{ave_i}	Average main and auxiliary engine power of ship i in kW
v_{ave_i}	Average cruising speed of ship i in nautical miles per hour

Table 4.4: Range attainable

Then the amount of fuel stops, η_{refuel} is calculated with:

$$\eta_{refuel} = \frac{L_{max}}{R_i} \tag{4.6}$$

L_{max} is the distance of the longest leg of a voyage. The R was used as a radius to screen for potential ports for additional refuelling. It is important to establish which ports are able to supply ammonia.

4.4.2. Engine type

The model discussed above is primarily dependent on the engine type and power of the vessels in the scope, as well as the route the vessels are sailing. In the next chapter 5, the operational profile and engine options are discussed to get a better understanding of the options currently and in the future available for sailing on ammonia.

4.4.3. Port

Due to the transport of ammonia as fertiliser, a global grit of ports that can handle ammonia is already in place. However, bunkering infrastructure is still a barrier [28]. This is however a key aspect in the development of all alternative fuels. A major issue is that ports are concerned about loss of competitiveness and the additional costs of regulations. The study of Vogelzang [86] looked into possible future scenarios for alternative fuels for the short sea shipping sector in Europe and what the effects of different policies have on the implementation. The research is done with an agent-based modelling approach created by Bas et al. [4], which represents the maritime fuel system. This model, the Maritime Fuel Policy Exploration Model (MarPEM), is used to study the effects of policies on development of alternative fuels. Vogelzang has made a number of suggestions to improve the performance of the model, such as adding the uncertainties of fuel prices, investment costs and regulations. The study points the uncertainty in fuel prices as the most important uncertainty in the deployment of emission abatement technology. For short sea shipping are the technological uncertainties such as space requirements and investments costs not expected to have a significant impact.

This study is to some extent an integral approach on the implementation of alternative fuels. The research looked into the connection of technological uncertainties and the policies on the port side. As mentioned in the research, it is expected that when more ports provide a fuel, more investment take place in the propulsion technology, since the risk of not being able to bunker is reduced. The study also briefly describes the production and the current availability of the fuels. However, ammonia is not included in this research. Additionally, as mentioned looked Vogelzang [86] into the effects of policies on short sea shipping. This thesis looks into the effects of deep sea shipping.

4.4.4. Production

A crucial critical success factor for the implementation of ammonia as a marine fuel is the availability of the fuel. Currently, all ammonia made is either grey (made with conventional energy source) or blue (made with conventional energy source and carbon capturing and storage). Production plant for green and hybrid ammonia is not yet available. This is partly due to the Haber Bosch reactor that is not yet commercially available. Also, investments are needed to either converse an existing production plant or build a new one. First, an estimation is needed of how much ammonia is currently produced and how much is needed to fulfil marine energy demand in 2030. Then the investment costs can be determined. Chapter 8 discusses both barriers.

PFP index

In order to evaluate ammonia on energy basis the power-to-fuel-to-power (PFP) index is used, which gives the ratio of the available output power from a fuel's combustion to the energy required in production. This index is calculated with formula 4.7. Here is $\eta_{combustion}$ the combustion efficiency. Figure 4.2 gives the material flows of the process. The materials entering the system are air and water. Departing is oxygen from water splitting, byproducts of air separation, water from fuel synthesis and combustion wastewater. For ammonia the PFP is 35% using an $\eta_{combustion}$ of 53%, which is significantly higher than methane (27%) with an $\eta_{combustion}$ of 54.1%. The distribution distance used in this index of 1600 km, is seen as the worst-case scenario. Grinberg et al. however states that this impact is relatively low compared to the other factors.

$$PFP^{atm} = \frac{\text{energy density} \cdot \eta_{combustion}}{\text{Water splitting} + \text{air separation} + \text{synthesis} + \text{distribution}} \tag{4.7}$$

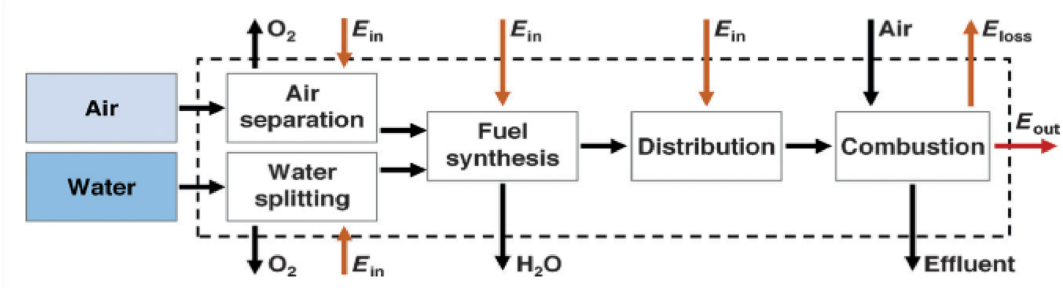

Figure 4.2: Material and energy flows in PFP system [32]

Grinberg et al. [32] only addresses the energy sector, including the chemical production process and the energy basis on power-to-fuel-to-power (PFP) index. They argue that other factors are important in addition to the PFP index to evaluate fuels, such as the techno-economic and environmental life-cycle assessment infrastructure aspects, interaction with other sectors, toxicity, handling safety and chemical stability. Another factor that was not discussed is the storage of ammonia.

5

Power plant configuration

This chapter discusses the first research question:

For which operational profiles and power plant installations is ammonia applicable?

This question encompasses power plant configuration and the impact on design of ammonia as a marine fuel. First the operational profile of the vessels in the scope is discussed, followed by a description of the most applicable power configuration options (ICE and fuel cells). The second part entails research into the impact on design, including toxicity of ammonia and the rules and guideline for the design.

5.1. Operational profile

With experience in implementation of LNG, methanol and LPG in the marine industry, it is safe to assume that the first vessels to sail on ammonia will be the vessels carrying ammonia [43]. These vessels already have the knowledge of handling the fuel [36]. In 2019 there were already over 200 ammonia carriers [25]. Interest for ammonia has also been shown for multiple ship types, particularly for deep sea container ships and bulk carriers. These vessels sail on a fixed route between two ports and have less variation in ports that need to supply ammonia. The vessels also sail long over distances and therefore have a great fuel demand [71]. For utility vessels the switch to ammonia comes with significant difficulties/challenges. Utility vessels are often located at one location for a certain period of time and are therefore very dependent on the location of the source of the fuel. In the future when ammonia could be available worldwide, these vessels can switch as well, but in the first stages of implementation, this isn't viable.
The largest oceangoing vessels (over 5000 mt) will in the near future need to comply with an energy label. This label will be instated in 2026 to further visualise the rate of pollution stemming from the marine industry. The vessels that score too low three years in a row need to improve to reduce emissions. Oceangoing vessel are mainly sailing on HFO. The requirements of the energy label are still under construction and will be delivered in 2021. From then on, the vessels will be examined, but only from 2026 on a too low rating will have consequences. The energy levels are just as with homes in the Netherlands, between A and E. If the vessels scores a D or E three years in a row, the vessel needs to change in order to be allowed to keep sailing. It is expected that a large number of vessels need to become more sustainable in order to be allowed to keep sailing [73].

Ammonia carrier

An ammonia carrier has a preference for efficiency over power density. The study of De Vries [24] saw in reference vessels that saving fuel costs is more important than required space and mass for power generation system.
Implementing ammonia as a fuel comes with a number of challenges. This first is the availability of a suitable engine. Secondly, ammonia is a toxic substance, which isn't allowed to be used as a fuel. This is inconvenient, since ammonia carriers are expected to be the first to convert to the use of ammonia. This rule is primarily in place to protect the IGC code. When ammonia is used as a fuel as well, it will be stored closer to people on board and the code must therefore be stricter. The code should refer to the IGC code for sailing on ammonia. Section 5.5 will discuss this further.

The number of ammonia carriers currently operational is quite small with 200 vessels [25]. This group might not be able to enforce IMO to make rules for sailing on ammonia. Another group to be able to make IMO make the rules are engine manufacturers who want to develop ammonia engines.

Container vessels
For container vessels this thesis looks at the larger sizes, since they have the biggest impact on the implementation of ammonia. These vessels sail mostly the same route and are therefore most likely the first to switch to ammonia since the infrastructure is in place sooner. Table 5.1 summarises data available from 2019. Averaging the smallest group over the gross tonnage of 26,299,000 Gt, this is approximately 12,000 GT [81]. Container vessels use often low-speed two-stroke diesel engines [90].

Gross Tonnage	Container vessels
500 - 15,000 GT	2,241
25,000 - 60,000 GT	1,555
> 60,000 GT	1,463

Table 5.1: Amount of container vessels per gross tonnage

Bulk carriers
Bulk carriers are often build for one contract and only sail on this route their whole lifespan. Bulk carriers often sail one way fully loaded and empty back. This sub sector can therefore switch easier since it only requires ports with available ammonia on few locations. However, bulk carriers are the most competitive market in the marine industry. This influences the switch to another fuel when it is more expensive. Table 5.2 shows the data from 2019 [81]. Bulk carriers also often are equipped with low-speed two-stroke diesel engines with a rpm between 60 and 190. These engines have the advantage of a direct connection to the propeller shaft without a gearbox. The engine has a lower power density compared to medium/high speed 4-stroke engines. [24].

Gross Tonnage	Container vessels
500 - 15,000 GT	3,807
25,000 - 60,000 GT	6,410
> 60,000 GT	1,778

Table 5.2: Amount of bulk carriers per gross tonnage

5.2. Power generation

While researching the optimal engine configuration for ammonia, internal combustion engines (ICE) (with both the compression ignition (CI) and spark ignition (SI)) as well as steam turbines, gas turbines, fuel cells (with proton exchange membrane (PEMFC), alkine (AFC) and solid oxide fuel cells (SOFC)) were researched. Figure 5.1 shows all options and fuel mixtures applicable.

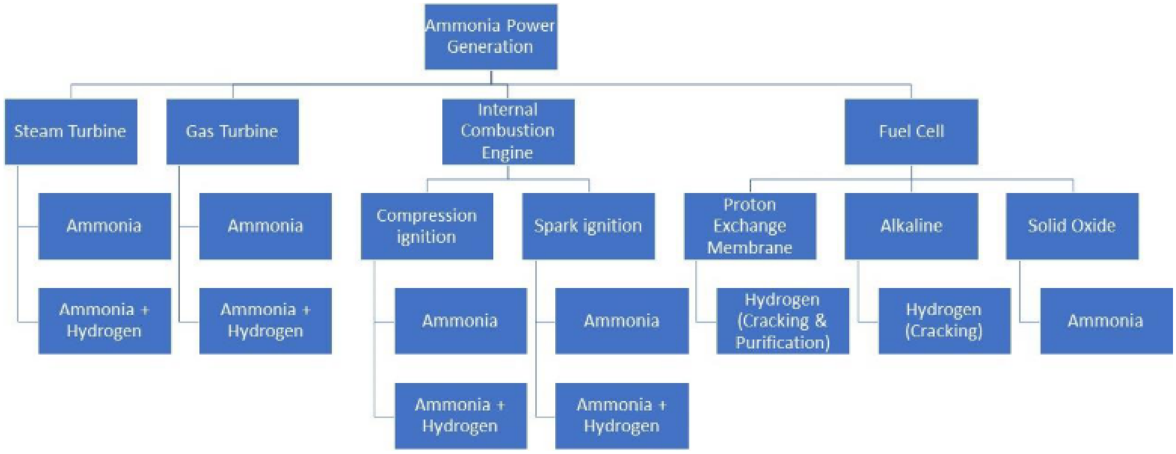

Figure 5.1: Engine options [24]

The research of De Vries [24] concluded that only the internal combustion engine while using an ammonia hydrogen mixture and the three fuel cells are feasible for marine applications. The other configurations are therefore not discussed further.

Combustion

Combustion of pure ammonia is challenging and ignition is more difficult than with conventional fuels. Auto-ignition temperature is high, 651°C, flame front speed is low, the fuel has narrow flammability limits of 15-28 % by volume air and a high heat of vaporisation (amount of energy that must be added to transform a liquid into gas). The flammability limit is the area between the lower and upper bound in which the fuel concentration is such that the ammonia and air mixture will burn. These combustion properties improve significantly if hydrogen is part of the mixture. This can be achieved by partially cracking the ammonia before injection [24]. The lower heating value of ammonia is 18.6 MJ/kg. The basic reaction during combustion is as follows: first the mixture is ignited, one being with pure oxygen and secondly with normal air with oxygen and nitrogen. The other gasses in the air are not considered since oxygen and nitrogen already constitute 99% of the volume in air.

$$\begin{aligned} 4NH_3 + 3O_2 &\rightarrow 2N_2 + 6H_2O \\ 4NH_3 + 11N_2 + 3O_2 &\rightarrow 13N_2 + 6H_2O \end{aligned} \tag{5.1}$$

The reaction with hydrogen is given below.

$$2H_2 + 4N_2 + O_2 \rightarrow 4N_2 + 2H_2O \tag{5.2}$$

The reaction equation produces only nitrogen and water [5]. This is however only in an ideal situation. Untreated exhaust gasses also consists of levels of NO, NO_2 and NH_3 that are too high. These exhaust gasses need to treated to extract these particle. This process is more complex than the SCR system that is used for conventional fuels. This system is discussed in more detail below.

5.2.1. Internal combustion engine

Research has shown that the most viable way to use ammonia as a fuel is in an internal combustion engine (ICE). In the engine first a catalyst is used to crack a small part of ammonia into nitrogen and hydrogen. The hydrogen is then after a compression stroke used to ignite the ammonia [33].
The total engine efficiency is the total of the thermal efficiency and the mechanical efficiency. The thermal efficiency is dependent on the induced power, fuel consumption (mass flow) and specific energy of the fuel. The induced engine power is based on the same number of cylinders, stroke volume, mean effective pressure, rotational speed and stroke type. There is no difference between using ammonia/hydrogen or natural gas. The fuel consumption in terms of mass flow is different for ammonia than conventional fuels due to lower specific energy. An ammonia/hydrogen mixture of 50%vol ammonia and 50%vol hydrogen has similar properties as methane in flame stability and flame front speed. Power density is dependent on rate of heat release and stability of the flame to propagate. Natural gas is 90% methane, so the energy consumption

[kJ/kWh] of both fuels is similar. The induced engine power is also the same, so the thermal efficiency is similar. The mechanical efficiency is also expected to be the same since there are no fundamental changes to the design of the engine that alter the mechanical design and operation. In conclusion the total engine efficiency is similar for ammonia and natural gas. The total engine efficiency ranges between 30-36% for spark-ignition and 40-47% for compression-ignition [16], depending on the point of operation for an ammonia-hydrogen mixture. When using pure ammonia the efficiency is increased to 51.6%, due to losses in thermal energy are reused to crack ammonia into hydrogen [24].
Contemporary internal combustion engine are very efficient, practical in operation and of proven technology. An ICE is less expensive, more robust with acceptable power density and better load response than a solid oxide fuel cell (SOFC) [24]. In comparison to an ICE with conventional fuel the ammonia ICE performs quite similar regarding power density, load response, part load performance and system efficiency [24].
In an internal combustion engine (ICE) the combustion of fuel occurs with an oxidiser in a combustion chamber. The expansion of the high-temperature and high-pressure gases produced by combustion exercises a force directly on the pistons of the engine. Chemical energy is hereby transformed into mechanical energy by the force moving the piston over a distance. There are two ignition options for an ICE, viz. through compression ignition and through spark ignition. For both configurations the options for pure ammonia and an ammonia-hydrogen mixture are discussed below.

Compression ignition ICE
With compression ignition the latent heat that is built up by highly compressing air inside a combustion chamber is used to ignite fuel. For conventional fuel the volume of air inside the chamber is compressed to a ratio of approximately 21:1. This high level of compression results in a high heat and air pressure in the chamber before the fuel is injected by a nozzle [31].
The first researches into igniting pure liquid ammonia revealed the need for a compression ratio of the engine of 35:1 with a jacket and an intake air temperature of 150°C. Recent study showed when igniting pure ammonia, the compression ratio of the engine intake air can be reduced by introducing a two stage injection, namely first a pilot fuel injection followed by the main injection. With a compression ratio of 30:1 approximately 90% combustion efficiency is achieved for all main injection timing conditions. This is significantly lower than the combustion efficiency of >98% of natural gas. This causes a lower efficiency compared to natural gas. NO emissions in this configuration are reduced by 25% compared to the previous method. However, there is a sizeable ammonia slip present. This can be prevented by precisely adjusting the pilot fuel injection, which also further reduces NO emissions.
A lower compression ratio (16:1) and a more stable combustion process is achieved while using an ammonia and hydrogen mixture of 70%vol ammonia and 30%vol hydrogen in a Homogeneous Charge Compression Ignition (HCCI). While using the mixture a trade-off has to be made between high compression ratio that is required to ignite ammonia and a reduced compression ratio to prevent hydrogen from ringing. Ringing is when the combustion intensity is too high causing a gas expansion at the speed of sound which causes oscillations in the cylinder. The same consequences happen with spark ignition, though with slightly different mechanisms. To monitor the most optimal ratio, an electric motor can be coupled to the engine to set the rotational speed at a fixed pace.

Spark ignition system
Ammonia is more difficult to ignite than conventional fuel. When using a spark plug based ignition system, ignition can be improved by adding stronger igniters, compacted combustion chamber and stronger spark plugs. Toyota has patented the combustion of pure ammonia with several plasma jet igniters or plural spark plugs to ignite ammonia at several points in the combustion chamber. However, pure ammonia ignition is not yet realised. Computerised models indicate that the optimal compression ratio for pure ammonia is 15:1. In these conditions the (unburned) ammonia slip is reduced by 8%, NO emissions are reduced by approximately 800 ppm and hydrogen slip is reduced with approximately 4000 ppm, because it is dissociated from ammonia. Igniting an ammonia hydrogen mixture with a spark ignition system is also an option. In conclusion ammonia can be used in combination with a spark ignition with possibly a combustion promotor, which could be hydrogen. Lhuillier et al. [46] researched a single-cylinder spark-ignition engine fueled with an ammonia/hydrogen/air mixture with various hydrogen fractions, equivalence ratios and intake pressures.

Compression rate:
Due to the higher octane rate of ammonia and hydrogen in comparison to gasoline a higher compression ratio is possible. Since flame front velocity and minimum ignition energy for ammonia and hydrogen are quite different, the philosophy behind a mixture was that an optimal value could be obtained. The ratio mainly depends on load and less on engine speed. The combustion is increased by adding hydrogen to the air-ammonia mixture. The exhaust pollutant emission (NO_x) has a maximum of 1,700 ppm at full load and 3,000 rpm, which is rather low.
In a recent study [46] a single-cylinder spark-ignition engine is fueled with a gaseous ammonia/hydrogen/air mixture with various hydrogen fractions, equivalence ratios and intake pressures. A small hydrogen fraction is used as a combustion promotor which can be generated by heat-assisted dissociation or NH_3 catalytic. This research has shown that ammonia is a suitable fuel for the SI engine with a high power output with achieved efficiencies higher than 37%. This set up takes advantage of the promoting effect of supercharging and hydrogen enrichment around 10% volume.
Another value observed during the research in fuel-lean and fuel-rich conditions are the NO_x and unburned NH_3 concentrations. A hydrogen-rich fuel promotes the NH_3 combustion efficiency and reduces the exhaust concentrations, but also promotes NO_x formation due to the higher flame temperatures. To prevent this process it is recommended to take advantage of the exhaust heat, NO_x and NH_3 in an after-treatment device [46].

5.2.2. Fuel cells

Another configuration to use ammonia is a solid oxide fuel cell (SOFC). Research shows that the fuel cell is the most efficient way to use ammonia. Fuel cells convert chemical energy through oxidation into electric energy with a high efficiency and zero emissions. This pollution-free power source however, at this moment does not deliver enough power to drive an ocean going tanker [5]. To be able to supple enough power multiple stacks are needed. The fuel cells are modular and can be stacked anywhere across the ship. One fuel cell delivers approximately 100 kW. Fuel cells have already been used widely in submarines. In this application the ammonia is split fully and the hydrogen is used to generate electric energy [33].
A fuel cell exists out of a tank, a gas processing system and a fuel cell stack that converts chemical energy into electrical energy through electro-chemical reactions of fuel with an oxidising agent, such as oxygen. Fuel cells require a constant source of fuel and oxygen to sustain the chemical reaction and as such differ from batteries. One of the challenges when using ammonia in a fuel cell is that the conventional membrane, the proton exchange membrane that is used in hydrogen fuel cells, is not suitable [79]. This can be solved with the use of a hydroxide exchange membrane fuel cell (HEMFC). With this membrane the capacity of the fuel cell is increased to a maximum of 135 milliwatt per centimeter squared by working at a higher temperatures which accelerates ammonia oxidation. With this increase the fuel cell performs nearly as good as the fuel cell with hydrogen. The reason why ammonia fuel cells deliver less power is because ammonia is more difficult to oxidise than hydrogen [77].
Two most promising fuel cells will be discussed in this section, viz. the proton exchange membrane fuel cell (PEMFC) and the solid oxide fuel cell (SOFC). Also the alkaline fuel cell (AFC) is discussed since it is an intermediate solution between the PEMFC and the SOFC [24]. An electrical efficiency of 50-60% is expected, depending on the fuel cell configuration. Some fuel cells operate at high temperatures which makes heat recovery possible and increasing the overall system efficiency to over 80%. However, low operational temperature fuel cells are more tolerant of dynamic load variations [28].

Proton exchange membrane fuel cell (PEMFC)
These fuel cells have been used in multiple modes of transportation such as cars, buses, light trains and submarines. Using ammonia in this fuel cell comes with a number of challenges. First, the conventional membrane of the PEMFC is affected by ammonia and is therefore not suitable. Also, this fuel cell can only convert pure hydrogen into electricity, so ammonia must be cracked and purified first. This costs energy.
PEMFCs are practical power generation devices that minimise in both space and weight. The fuel cell is stacked in layers to minimise the required area for the gas, electrode and electrolyte to meet. The layers are porous and are lined up together in the order cathode, electrolyte and then anode. These three parts are fitted between two bipolar plates. The PEM plate only allows protons (H^+) to pass through. This plate is made of Nafion which operates on low temperature between 60 and 80 °C and can handle quick start and stop without degradation. This means it can be used in situation where speed is frequently changed. The bipolar plates allow entrance to oxygen and hydrogen through the channels and discharge the produced water. The only

waste products are water vapour and heat. The thermal efficiency of the PEMFC lies between 50 and 60%, which is significantly higher than the 30% of the diesel ICE. This efficiency can be even higher if the excess heat is re-used elsewhere in the energy production process. PEMFC are most efficient at 25% rated power and have a fast start-up time of 0-100% in 5-10 sec and low-100% in 1 sec. [60].

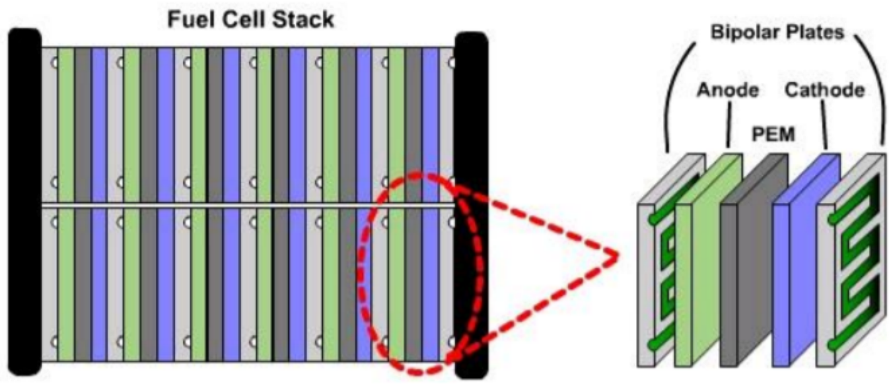

Figure 5.2: Layout layered PEMFC [60]

The PEMFC has sufficient load response characteristics for fluctuations in the operational profile such as heavy weather and sailing in the port. As mentioned multiple fuel cells are needed since one fuel cell only delivers 100 kW. The idle power ranges between 10-20%. This means that 10-20% of the total power is the minimum power that is required at all times. If this falls below the lower limit, a number of fuel cells can be switched off. This is also the case for the other fuel cells discussed below. The PEMFC are sensitive for air pollutants and salty air, which can affect the performance of the fuel cell. It is therefore recommended to use air filtration in the air supply.

Alkaline fuel cell (AFC)
The Alkaline fuel cell also only runs on hydrogen, so ammonia needs to be cracked first. This system, however, does not require purification of the fuel. As well as the PEMFC does the AFC work on low temperatures and the principle is similar to PEMFC. However, the AFC is not as often used as the PEMFC even though the technology is proven. The load response of the AFC is approximately 16% Pmax/s. The AFC is sensitive for CO_2 poisoning and therefore air treatment by CO_2 scrubbing is required. The efficiency of the fuel cell lies between 50 and 60%. An AFC has been developed by GenCell that can crack ammonia while in process. The first commercial application of this system was in July 2018. Another party, ZBT also developed a system with non-electrical cracking.

Solid oxide fuel cell (SOFC)
The SOFC is of similar design as the other fuel cells, but is however able to process ammonia directly without cracking or purification. The electrochemical response of the SOFC is adequate, but slow due to thermal response. The average is 0.003%P_{max}/s. Also the start-up time of the SOFC is multiple hours.
The SOFC is less sensitive for impurities. These fuel cells are however not yet on the market but are only used for lab experiments and have only been tested on ships. There it was concluded that the acceleration and the salty air were no issue for the SOFC. In general, the efficiency lies between 50 and 60%, but efficiencies above 60% have also been reached. Research has proven the process to be highly efficient and without NO_x formation. This fuel cell is the most efficient, but has some challenges to overcome such as power density and load response capabilities. Additionally, the total cost of ownership is higher than the ICE and the savings on the OPEX could take too long for the fuel cell to be the better option.

Split ammonia

The cracking of ammonia to produce hydrogen is done by passing ammonia through a heater and then over a catalyst bed to oxidise ammonia to split the endothermic decomposition of ammonia into hydrogen and nitrogen. Currently cracker technology is available for 1-2 ton/day range for companies. Smaller cracking is not yet commercially available. The challenges for cracking are first the nickel-based catalyst that is used in

existing crackers. This method is not efficient and required high temperatures. There is research ongoing on ruthenium, cobalt and lithium catalysts that can operate on lower temperature to replace the nickel-based option. The second challenge is the proper heat transfer to the catalyst when the crackers are getting larger [7].
Another method to split ammonia is plasma decomposition. This method is still in the research phase. Here hydrogen is produced from ammonia with electrolysis. An alkaline electrolytic cell is used to couple ammonia electro-oxidation and hydrogen evolution. However, this process is too slow for practical implementation [7]. The heating, cracking and post polishing (removal of residual ammonia) causes energy losses and the available energy of hydrogen from cracked ammonia is similar to original ammonia. With 1 ton ammonia, 2% will be used to operate the selective catalytic reduction (SCR) to reduce NO_x and NH_3 from the exhaust gasses and the remaining 98% will produce 16,530 MJ of energy. The same 1 ton ammonia produces 0.18 ton hydrogen, which is equivalent to 19,205 MJ energy. However, due to 15% of the energy required for cracking and processing operations, the energy production is 16,626 MJ.

5.2.3. Conclusion power generation

ICE have a high efficiency and are sufficient practical. The SOFC has a higher efficiency than the ICE but lacks power density, load response and is too expensive. PEMFC and the AFC are less efficient than the ICE. Also the ICE possesses better power density and load response properties. It is clear that the ICE is currently the best option.
In comparison with the ICE on fossil fuel an ICE ammonia option has similar technical performance on power density, load response, part load performance and system efficiency. Added to this, an ICE option has less detrimental emissions. However, as mentioned in chapter 2 the ammonia option is around 3.2 times more expensive than a conventional one. This is calculated with a price of 850 euro per ton ammonia and 500 euro per ton low sulphur 0.5% HFO. In the future the difference may turn the other way, for instance of the price of ammonia drops to 400 euro per ton, and the HFO remains at 500 euro per ton but will come with a mark-up CO_2 taxation of 100 euro. All options are feasible, but pure ammonia combustion has its limitations in performance in comparison to an ammonia hydrogen mixture.
All three fuel cells are viable options with the SOFC being the most efficient. However, with the significant higher CAPEX, the second option of the ICE is often made. The fuel cell has a higher efficiency, but lacks power density, load response and is more expensive than the ICE.
Challenges surrounding fuel use and combustion include avoiding ammonia slip and managing nitrous oxide (NO_x) emissions. To prevent this the engines are expected to complete a diesel-cycle combustion; including compressing air, igniting a pilot flame and then injecting ammonia to ensure a stable ignition and full combustion. The ships also need a selective catalytic reduction (SCR) to minimise escape of emissions from ammonia combustion [71].
For all power generation options a lot more research is needed before the development stage is reached. The current options are not able to run on ammonia. This also entails a higher cost than conventional power generation options. There are a number of options in development, all in different technical readiness levels. These are discussed in the paragraph below.

5.2.4. Engine options

Now that the engine type for the vessels in the scope are known, the commercial available options are discussed, as well as the costs involved. The first option is the MAN ES dual-fuel engine.

MAN ES dual-fuel engine

The risk associated with designing a power system for a fuel that is not yet worldwide available are significant. With the application of a dual fuel engine the vessels maintain fuel flexibility. The engines have a higher upfront cost, but are likely to be beneficial in the long run. MAN Energy Solutions aims to have a two-stroke dual-fuelled ammonia ICE ready in 2024 for large scale container ships, followed by a retrofit package for rebuilding existing vessels. Figure 5.3 shows the road map to achieve this goal. This engine offers fuel flexibility with the simultaneous use of gas and liquid fuel. The amount of gas consumption is fixed and the liquid fuel is used to reach the desired output. This allows the operator to find the best balance between CO_2 reduction, cost and fuel availability.
Developing the engine comes with a number of challenges. Ammonia is toxic and potentially corrosive. MAN ES is therefore focusing on the creation of a complete and safe system from fuel tank to engine. Such a system includes double walled tanks which are being tested with different materials, smart software and optimal pro-

cess solutions. Another challenge is preventing nitrous oxide (N_2O) to be emitted. MAN is also researching four-stroke ammonia engines. This model of engine will likely also need selective catalytic reduction (SCR). Combustion of ammonia produces no CO_2 or SO_x and only produces negligible amounts of soot and ppm. It however does produce NO_x, N_2O and a possible ammonia slip. Post treatment of the exhaust with a SCR will eliminate the nitrogen byproduct. In this process ammonia itself is used as a reducing agent, so storage and handling of specific chemicals on board is not needed which cuts significantly costs. The SCR for removing NO_x and N_2O is already commercially available and the costs similar to the costs of a SCR for conventional fuels.
The expected extra investment for the ammonia fueled engine is estimated to be 30% in respect to an equivalent unit. Additional investment is needed for storage tanks and LFSS, which is discussed further in paragraph 5.2.5. The cost of SCR is compared to the cost of a cracking unit. The SCR costs are extrapolated from a number of power plant installations. The impact of initial flue gas NO_x concentration on the costs are estimated by the EPA Air Pollution Control Cost Spreadsheet. The cost of ammonia crackers are uncertain, since the larger sizes are not yet commercially available. The costs are obtained from alternative fuel studies. The cracker and SCR are calculated for 1000 tpd (tons per day). If the engine develops into a NO_x outlet similar to current operations on natural gas, the SCR installation is the cheaper option. However, when the engine reaches the documented 1000 ppm NO_x for turbine operations, the calculated costs of the SCR unit to remove these high levels indicate that ammonia cracking for larger quantities is the more economical choice. This is only looking into the two systems and not into the production of ammonia [7]. [11].

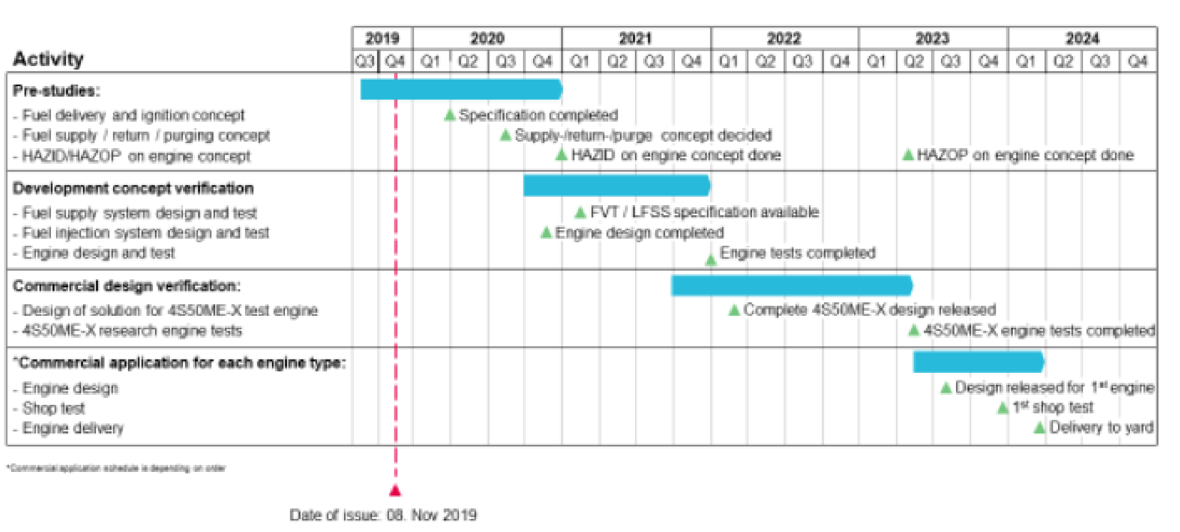

Figure 5.3: Road map ammonia development project MAN [43]

AmmoniaDrive

De Vos [23] conceptualised a hybrid internal combustion engine-solid oxide fuel cell, the AmmoniaDrive. This power/propulsion plant solution is single-fuel, high-efficiency and high-tech which will produce no pollutant emissions. Figure 5.5 shows the preliminary lay-out of the power plant. This power plant consist of a solid oxide fuel cell which produces hydrogen, which is fed into the internal combustion engine. The power plant contains further a selective catalytic reduction (SCR) to reduce NO_x and NH_3 from the exhaust gasses. This set-up is inspired on the Dutch invention GasDrive, which is a hybrid power generation system with an ICE that runs on anode-off gas of the SOFC and additional fuel. This set-up increases the total power-generation efficiency with 5 to 8% compared to an ICE-only power plant. This efficiency difference depends on the power split between the ICE and SOFC and the applied heat integration. The 5% efficiency increase is due to a high P_{ICE}-to-P_{SOFC} ratio. This is a relatively large engine compared to the SOFCs, which are a realistic power plant configuration regarding space and weight requirements, capital expenditure (CAPEX) and transient capabilities.
The difference between the GasDrive and AmmoniaDrive is that ammonia needs a promotor fuel to combust in an ICE because of the low flame propagation and combustion rate of ammonia. Hydrogen is an ideal promotor and is released in the anode-off gas due to internal reforming in the SOFC and fed to the ICE.

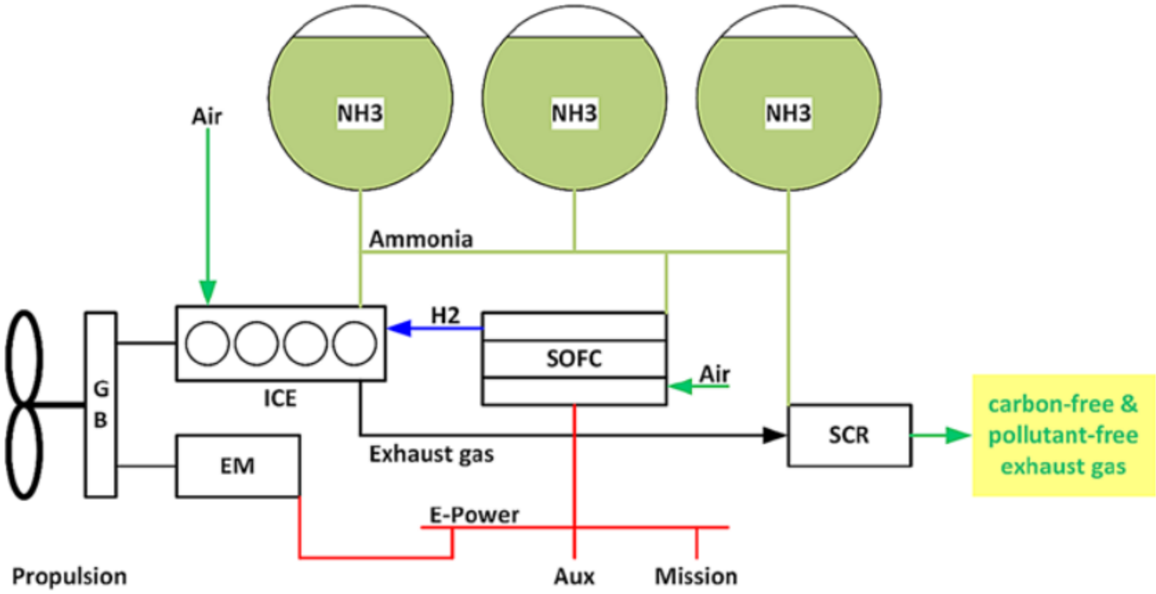

Figure 5.4: Ammonia drive system lay-out [23]

The implication of ammonia on board however still raises a number of questions regarding power plant configuration, whether it is the only fuel onboard, how the energy conversion efficiency can be obtained and how it could be improved. [23]

5.2.5. Other required systems

When using only ammonia, some equipment is not needed anymore, such as treatment used for HFO; High speed separators, heaters, boosters and a settling tank. Also a SO_x abatement system used for high-sulfur HFO is not needed anymore. Systems that are required are the Liquid Fuel Supply System (LFSS), SCR port treatment and other specific engine upgrading. These additions have a direct impact on CAPEX and OPEX. The LFSS system provides ammonia to the engine at the required conditions. This system can either be installed on deck or connected to the engine by double walled piping. If installed in the engine room an air lock system preventing diffusion of ammonia is required. The LFSS system can provide ammonia in liquid and gaseous phase. When provided as gas at low pressure this system is similar as the LFSS of LNG. When provided in liquid phase the system used for LPG on LGIP engines can be used with minor adaptations.

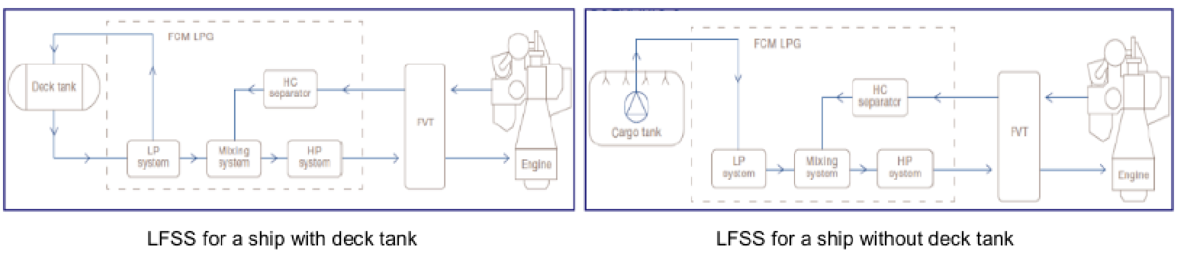

Figure 5.5: Block diagram ammonia LFSS [43]

The LFSS system;

- provides fuel at the required temperature and pressure to the engine regardless of the storage conditions
- segregates fuel from cargo without polluting the cargo from the engine
- operates the purging when needed

- handles recovery of the product from purging and minimise release in the atmosphere

5.3. Impact on design

The adaptations of the vessels already carrying ammonia consist of only the installation of a dedicated NH_3 fuel supply system and upgrading of the engine. The vessels not carrying ammonia also need to be refitted to be able to load and store ammonia. At the time of writing this thesis the design and safety regulations are not yet implemented in the IGF code, details are provided in section 5.5. This code will also include description of safe loading, storage and operation of the ammonia system onboard.
The type C pressurised tank is the most cost-effective system to store ammonia on board. This system has limited routes and installed power. The tank stores ammonia at ambient temperature and therefore does not require a liquefying system. The tank can either be installed on deck or integrated into the hull design. The limit of the tank is 2000 m^3 [43]. This method however assumes that the tank volume is available for ammonia only for the ships propulsion. This will not be feasible from the start.

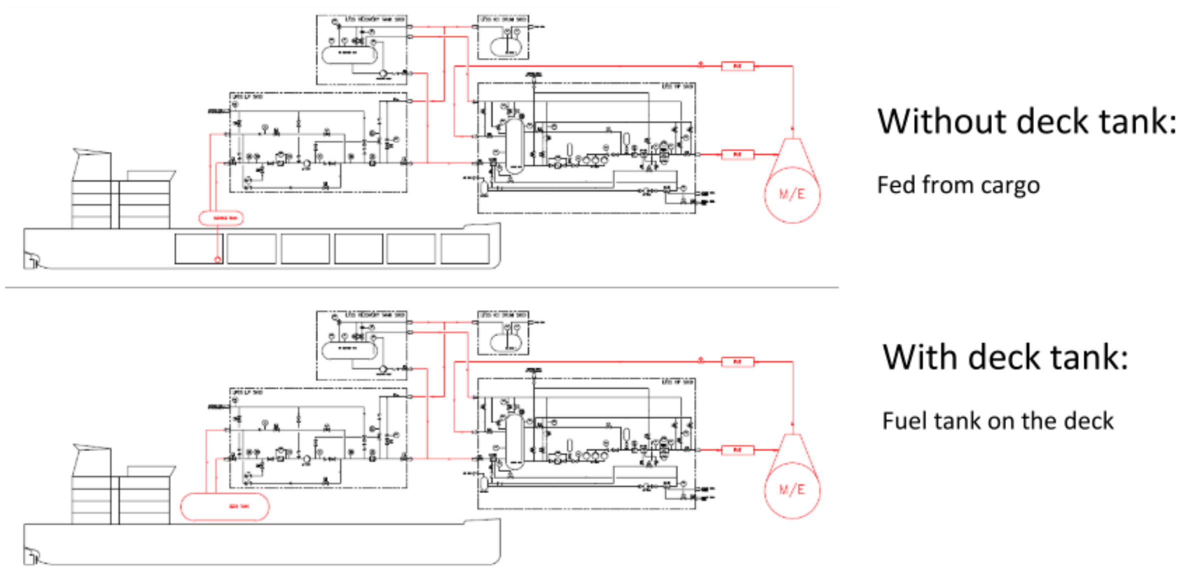

Figure 5.6: Ammonia fuel tank options [43]

An important difference between for example HFO or MDO and ammonia is that the energy density of ammonia is much lower, shown in figure 2.6. This means that for the same amount of power more fuel is needed. Ammonia has 40% of the calorific value of hydrocarbon fuels [76]. Due to the energy density difference the net storage volume of ammonia is approximately 70% larger than LNG [43]. This impact on the vessel is further discussed in chapter 6.

Other components

The impact on design consist of a number of components. First the technology related to ammonia usage is discussed, followed by the impact of switching to ammonia.
Additional to the engine set up there are a number of technologies that are needed when using ammonia. The following list summarises those components.

- Knock-out drums vent masts, pressure relieve system
- Fuel delivery / return valve-trains and lines
- Engine control - gas stop
- Automatic purging inerting of system lines
- Nitrogen generation /use on board

- Ammonia / gas detection
- Ventilation
- Ammonia oil-contamination.

5.4. Toxicity

Ammonia is toxic, corrosive, hardly inflammable gas with a strong odour. The threshold for detection of the odour is between 5 to 50 ppm of air. Ammonia in even small concentration can irritate the eyes, throat and airways but has no chronic effect on the human body. Ammonia reacts with and corrodes copper, zinc and many alloys. The only materials that can be used in tanks, fitting and piping when using ammonia are iron, steel, non-ferrous alloys, rubber and polymers. When using a nickel alloy the nickel content should be below 6% to avoid nickel crystalline corrosion. Oxygen levels over a few ppm in liquid ammonia can cause stress corrosion cracking in steels. The rate of corrosion increases rapidly with elevated temperatures.
Looking into the hazard statement from the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), ammonia fits into the following categories.

- H221 Flammable gas. Hazard category: physical hazard
- H280 Contains gas under pressure; may explode if heated
- H314 Causes severe skin burns and eye damage. Hazard category 1B
- H331 Toxic if inhaled. Hazard category: Health hazard
- H410 Very toxic to aquatic life with long lasting effects. Hazard category 1.

Various studies have looked into hazard identification and define design criteria with a risk evaluation. These studies also state that ammonia is not new in the marine sector and has been shipped as cargo and is used as refrigerant. The necessary practices have already been set in place, including operational and safety procedures. Rules are already in place for using ammonia on board, such as the International Code for the Construction and Equipment of Ships Carrying Liquefied Gas in Bulk (IGC Code) [43]. The next section discusses these codes.

5.5. Codes and regulations

At the moment of writing the technology for ammonia as a marine fuel is far ahead of the relevant legislation or regulations. Currently 17.5 million tons ammonia for mainly fertilisers and refrigerant is transported by truck, trains, ships and pipelines. The level of safety in this transport has proven to be high [43]. Engineering and chemical companies are providing key technical information to legislators to try to persuade to look into ammonia [71].
The development of the specific guidelines for ammonia as a marine fuel can be based on solution, devices and procedures yet in place for safe handling ammonia on board as well as the experience of LNG as a fuel. However, a detailed study in dispersion needs to be conducted to include in the codes. Anhydrous ammonia is lighter than air and will rise in dry air. In humid air ammonia will however react with water and remains close to the ground and limit dispersion into the environment [43].
As of 2019 the codes in place have explicit prescriptive rules for carrying and fuelling LNG. The other low flashpoint fuels need to be acceptable to the Administration, provided that the same level of safety is met as with natural gas (IGC) and oil-fueled (IGF). This same level of safety can be proved by a risk-based approach and literature study. The factors to research are leakage, accumulation, dispersion, explosion and risk assessment [25].

5.5.1. IGF

The IGF code is the International Code of Safety for Ships using Gases or other Low-flashpoint Fuels, effective since 1 January 2017. The IGF code is created when it became apparent that a mandatory code for ships using gases or other low-flashpoint fuel is needed, for ships greater than 500 gt. Smaller ships have a voluntary application. The code states mandatory criteria for the arrangement, installation, control and monitoring of machinery, equipment and systems for vessels to minimise the risk to the ship, crew and environment. This code was intentionally designed for LNG but soon will also contains requirements for methanol and ethanol.

Requirements for other low-flashpoint fuels will be added when developed by the IMO. This code provided rules concerning arrangement, installation, control and monitoring of machinery, equipment and systems using low-flashpoint fuels. The code is divided into a number of parts, namely, ship design and arrangement, fuel containment system, material and general pipe design, bunkering, fuel supply to consumers, power generation including propulsion and other gas consumers, fire safety, explosion prevention ventilation, electrical installations and control and monitoring and safety systems. The Fuel Containment system is the system for storage including tank connections. It also includes primary and secondary barriers, associated insulation and any separating spaces, such as cofferdams and any adjacent structure that is supporting these elements [41].

According to the IGF code is ammonia permitted if the equivalent level of safety is proved. The IGF code states that the fuel storage, handling and distribution system should be located in the cargo area and not in the engine room [25].

5.5.2. IGC

The ships also needs to comply with the 1983-2014 IGC Code. This is the International Code for the Construction and Equipment of Ships Carrying Liquefied gases in bulk [37]. For the use of ammonia the IGC code needs to be amended. The code currently prohibits the use of cargo identified as toxic product as fuel for the ship, this includes ammonia. As stated in 16.9.2. "The use of cargoes (as fuel) identified as toxic products shall not be permitted" [25].
This code focused on protection of personnel on board a gas carrier transporting ammonia. Listed below are a number of safety measures [43].

- Respiratory and eye protection devices for emergency escape purposes shall be provided for every person onboard, with some minimum requirements (no filter-type; self-contained breathing apparatus 15 minutes minimum duration)
- Protective clothing to be gas-tight
- One or more suitably marked decontamination showers shall be available on deck, depending on the size of the ship, and shall be able to operate under all ambient conditions

The IGC code for cargo tanks and pipelines, valves, fittings and other equipment that is in contact with cargo liquid states the following guidelines:

- Mercury, copper and copper-bearing alloys, and zinc shall not be used for cargo handling ammonia and for equipment normally in contact with ammonia liquid or vapour
- Maximum nickel content in steel is 5%
- The ammonia shall contain not less than 0.1% w/w water
- Minimum requirements for steel yield strength and post-welding treatment are indicated in IGC Code chapter 17.12

The IGC code (chapter 17.12) also indicates how to minimise risk of ammonia stress corrosion cracking. [43]

5.5.3. IBC

In order to sail on ammonia, the ships needs to comply with the IBC code. This is the International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk, Amended by Resolution MEPC.225 [37]. This code provides a standard for safe carriage in bulk by sea of dangerous chemicals and noxious liquid substances. It provides rules about the design and construction standard for ships. As of now the code doesn't include ammonia, only aqueous ammonia (an ammonia solution) up to 28%. The code is therefore not applicable.

5.5.4. Conclusion rules

The IGF Code allows non-ammonia carrying vessels to use ammonia as a fuel whereas the IGC Code prohibits the use of ammonia as fuel for ammonia carriers. This is a strange contradiction, since it is believed that these vessels will be the first to adopt ammonia as a fuel. The difference in the codes is that the IGC code includes

the whole ship, including the cargo tank (cargo requirements) and propulsion system in chapter 16, Cargo as fuel. The IGF code only includes the propulsion system [25]. The IGF code permits ammonia to be used if the equivalent level of safety is proved. The IGF code states that the fuel storage, handling and distribution system should be located in the cargo area and not in the engine room. The IGC code needs to be updated to be able to use ammonia as a fuel.
While the codes need to be updated for the use of ammonia as a fuel, some preliminary activities and risk assessment are carried out. First is looked into the characteristics of ammonia. Ammonia has a lower flammability than LNG, but has a higher level of toxicity. However, the industry already has experience with handling ammonia, which makes is possible to implement the fuel in the Code. The second assessment is of the required systems to use ammonia. Ships carrying ammonia as cargo and ships using it as fuel both only need an LFSS installation and storage system. Installing the systems on deck limits the risk in the engine room to only pipes from the LFSS to the FVT and the ammonia fuel pipes to the engine. These pipes should all be double walled. This lay-out secures an inner space in the engine room and prevents leakage and venting to the atmosphere. This technology is already in use with LNG but needs to be evaluated on toxicity. Finally, the study in dispersion needs to be included in the codes. However, all and all it is reasonable to state that a safe and environmental-friendly way to handle an ammonia-fueled ship can be achieved with the existing technology [43].

Timeline methanol
In the 94th session of the Maritime Safety Committee from the IMO in November 2014 the draft of the IGF code was approved, which came into practice on 1 January 2017. This draft relates to ships sailing on low-flashpoint fuels, initially only including LNG. The next phase was the inclusion of ethanol and methanol, which is discussed in the next meeting on September 2015. The sub-committee to discuss this addition is the Carriage of Cargoes and Containers (CCC). In the 5th session on September 2018 of this committee it is concluded that a draft will be made for the use of methanol. The amendments are adopted in the session on November 2020 [40].

[39] The sections referring to methanol include:

- Location of cargo and methanol fuel tanks
- Limit for safe location of fuel tanks
- Fire safety
- Ventilation, control and monitoring fire detection system in machinery spaces
- Drills and emergency exercises

Since the process of using ammonia is comparable to the process of methanol, it can be said that the implementation process could take the same time as of methanol. This means that even if ammonia is discussed in the next meeting in November 2021, the rules will be put in operation in approximately late 2024. However, the first step to include ammonia in the codes has not yet been taken, so the implementation will likely be much later than 2024. The engine is therefore likely to be available before the regulations.

6
Routing

This chapter discusses the routing and the energy demand of the vessels in the scope with the following sub research question.

To what extent does the shipping range of ammonia coincide with the current trading corridors?

In the literature study of this thesis a number of methods have been researched to map routes and energy demand. These methods all look at vessel specific data with data from AIS, Clarkson and/or Fearnleys. These methods are discussed in section 4.4.1. This chapter first discusses the most common routes for the vessels in the scope (ammonia carriers, bulk carriers and container vessels). Then nine case vessels in three most common sizes are researched to calculate the energy demand and required mass and volume to determine the effect of ammonia on the shipping range and whether and which vessels need to adapt.

6.1. Trade routes

As mentioned in chapter 5 the most likely to switch to ammonia first are the ammonia carriers, followed by bulk carriers and container vessels. The following figures show the trading corridors for these vessels. Figure 6.1 shows the ammonia trade routes and quantities of August 2020 and of the top figure container trade routes. Figure 6.2 shows the routes for transporting bulk of coal, grain and iron ore, which are the main bulk cargoes. The cargo in TEU moved on these routes is shown in table 6.1. The most travelled route lies in the East-West trade. This encompasses the Pacific and the Atlantic sea [80].

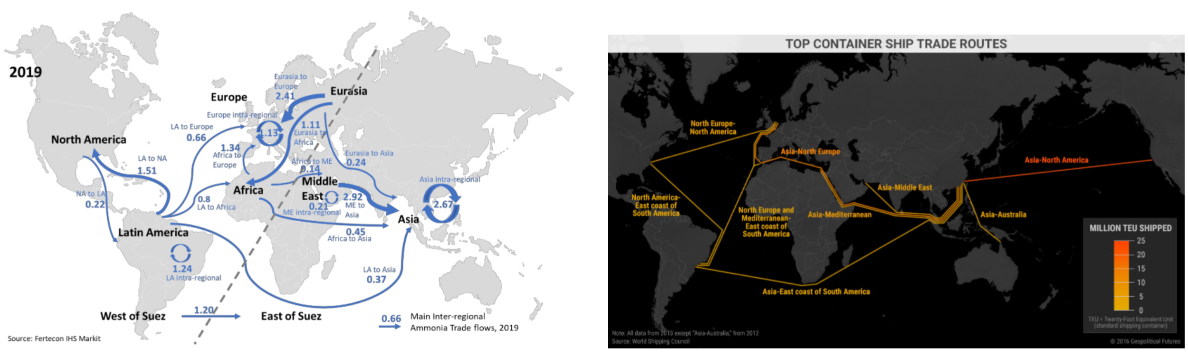

Figure 6.1: Left:Global ammonia trade in August 2020 [43]. Right: Container ship trading routes [82]

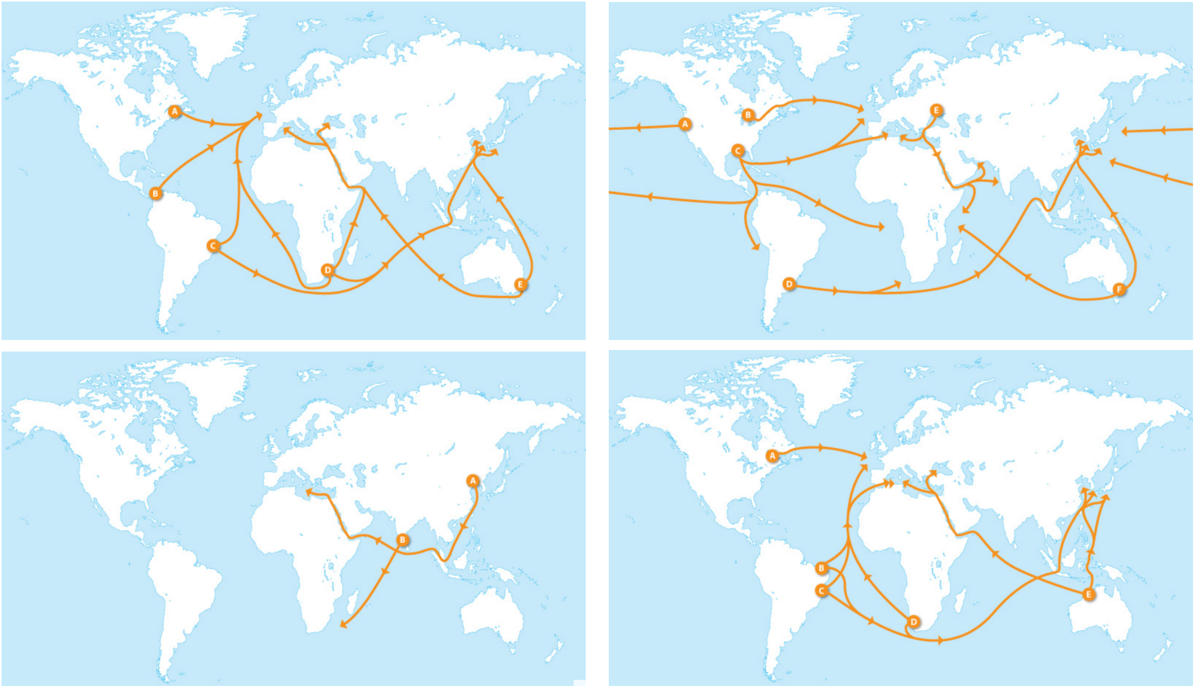

Figure 6.2: Bulk carrier routes; top left coal, top left and bottom left grain and bottom right iron ore [2]

Route	West Bound	East Bound	North Bound	South Bound	Total
Asia-North America	7,490,000	19,482,000			26,572,000
Asia-North Europe	9,924,000	5,139,000			15,063,000
Asia-Mediterranean	5,504,000	2,409,000			7,913,000
Asia-Middle East	3,340,000	1,400,000			4,740,000
North Europe-North America	3,284,000	2,120,000			5,404,000
Asia-East Coast South America			730,000	1,344,000	2,074,000
North Europe/Mediterranean - East Coast South America			830,000	850,000	1,680,000
North America - East Coast South America			794,000	474,000	1,268,000

Table 6.1: Top trade routes in 2017

As can be seen the routes for the three types of ships are very similar. The use of ammonia for agriculture has already generated a global network of ports where ammonia is traded and stored in 120 ports worldwide [36]. Figure 6.3 shows the transit ports of ammonia. A more clear image of import and export ports is shown in appendix B.

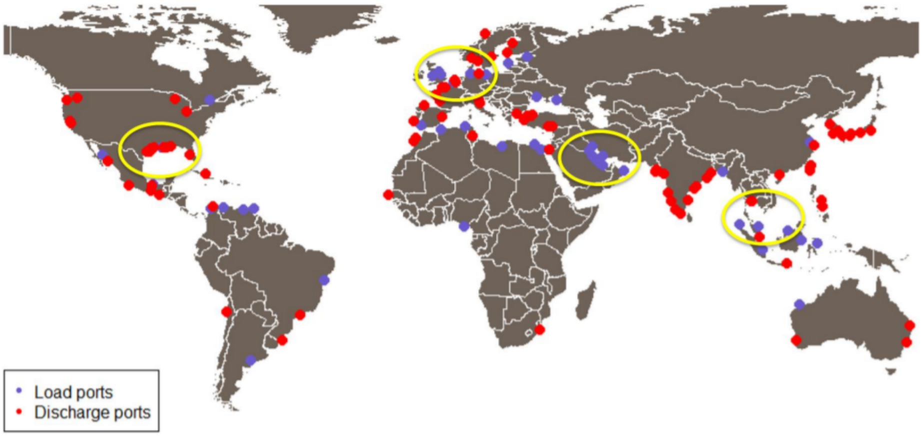

Figure 6.3: Worldwide ammonia ports [25]

As can be seen the ports that are able to handle ammonia are strategically located along the shipping corridors. This eliminates the need to build infrastructure to be able to store and supply ammonia in ports. Chapter 7 elaborates on this subject.

6.2. Case study

To be able to calculate the attainment rate of the type of vessels in the scope, a case study is performed with an number of existing vessels. First most common sizes for each type of vessel is discussed.

Ammonia carriers

Ammonia is transported either fully pressurised at 10 bar at 20°C, fully refrigerated at -34°C at 1 bar or semi pressurised/refrigerated. These three forms have a common capacity of 6,000, 18,000 and 54,000 DWT respectively. Table 6.4 shows the mean data in these sizes [24]. For the calculations three existing vessel have been chosen to determine the routing. These vessels are shown in table 6.3.

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

Figure 6.4: Three capacities for ammonia carriers [24]

Container vessels

For the container vessels the most common sizes for deep sea sailing are Panamax 8,000 to 15,000, Post-Panamax 15,000, Suezmax, Post, Suezmax and Post Malacamax. For the calculations three vessels have been chosen that all are deep sea sailing and of three different sizes, namely 15,000 TEU, 8,750 TEU and 5,652 TEU.

Type	Capacity (TEU)	Length	Beam	Draft
Ultra Large Container Vessel (ULCV)	> 14,500	> 366	> 49	> 15,2
New Panamax	10,000-14,500	366	49	15,2
Post Panamax	5,100 - 10,000	366	49	15,2
Panamax	3,000 - 5,100	294	32	12

Table 6.2: Container vessel sizes

Bulk carriers
For the bulk carriers there is a wide variety of sizes. Table 6.5 shows the most common options. For the calculations the Handymax, Panamax and Capesize are taken into account. Table 6.3 shows the ships chosen for the calculations.

Type	Deadweight, ton	Draught, m	LOA, m	Beam, m	Geared (Yes/No)	Number of Holds
Handysize	32,000	10.2	179.9	28.4	Yes	5
Supramax	52,000	12.2	199	32.2	Yes	5
Ultramax	62,000	13	200	32.24	Yes	5
Panamax	75,000	14.1	225	32.26	No	7
Kamsarmax	82,000	14.5	229	32.26	No	7
Post-panamax	98,000	14.6	240	38	No	7
Capesize	172,000	17.95	289	45	No	9
ULOC (Valemax)	400,000	23	362	65	No	9

Figure 6.5: Most common bulk carriers sizes [69]

The table below shows an overview of all vessels in the case study with the length, capacity, installed power and the distance of their longest route. Also the ports between the vessels sail in this case study are named.

Vessel	Length m	Capacity	Power MW	Distance nm	Start port	End Ports
Container vessels		TEU				
Emma Maersk	397	15,000	80.08	12,225	Ningbo, CN	Hamburg, GER
MSC Texas	334	8,269	68.6	6,604	Freeport, BH	Suez port, EG
Ever Urban	285	5,652	48.6	10,092	San Antonio, CL	HK
Bulk carriers		dwt				
NSU Carajas	361	399,688	24,6	15,302	Qingdao, CH	Sao Luis Anch, BR
Lowlands Blue	240	100,535	10.5	21,276	Huanghua, CH	Vancouver, CA
Darya Chand	200	63,590	8.1	15,241	Taicang, CN	Tampa, USA
Ammonia carriers		m^3				
Genesis River	230	54,149	16.7	15,078	Guangzhou, CH	Houston, USA
Yara Sela	160	20,600	7.6	5,215	Bordeaux, FR	Point Lisas, TTO
Renaud	112	7,535	4.55	457	N'Kossa, CG	Owendo, GA

Table 6.3: Case ships

6.2.1. Emma Maersk

The first vessel is the container vessel Emma Maersk and for this vessel the calculations are described. A typical route for this vessel is from Ningbo, China to Hamburg in Germany. To calculate the attainment rate of the vessel on this trip, the method described in chapter 4 is used. The range the vessel is able to sail is calculated with formula 4.4.1, shown here below again.

$$R_i = v_{avg_i} \cdot \left(\frac{\left(\frac{V_{NH_3 capacity_i}}{\text{fuel margin}} \right) \cdot D_{NH_3} \cdot \eta_{NH_3}}{P_{ave_i}} \right) \tag{6.1}$$

The first part is the average cruising speed, which is known. Also known are the fuel margin, which is 1.2 for all ships, and the efficiency of the engine which ranges between 49-52%. The lower efficiency is taken into account to have a more conservative fuel demand approach. The average main engine power is also known for the case vessels, so only the available space for the fuel system and the volumetric density of the system needs to be calculated.
The volumetric density of the system is calculated by multiplying the density of ammonia, which is 683 kg/m^3, with the energy density of ammonia, which is 5.2 kWh/kg. This leads to a volumetric density of 3,527 kWh/m^3. The available space is derived from the bunker capacity of the ship plus the engine volume. The bunker capacity is 16,920 mt, which leads to a volume of 16,752 m^3. The engine volume is derived from the equation in figure 6.6.

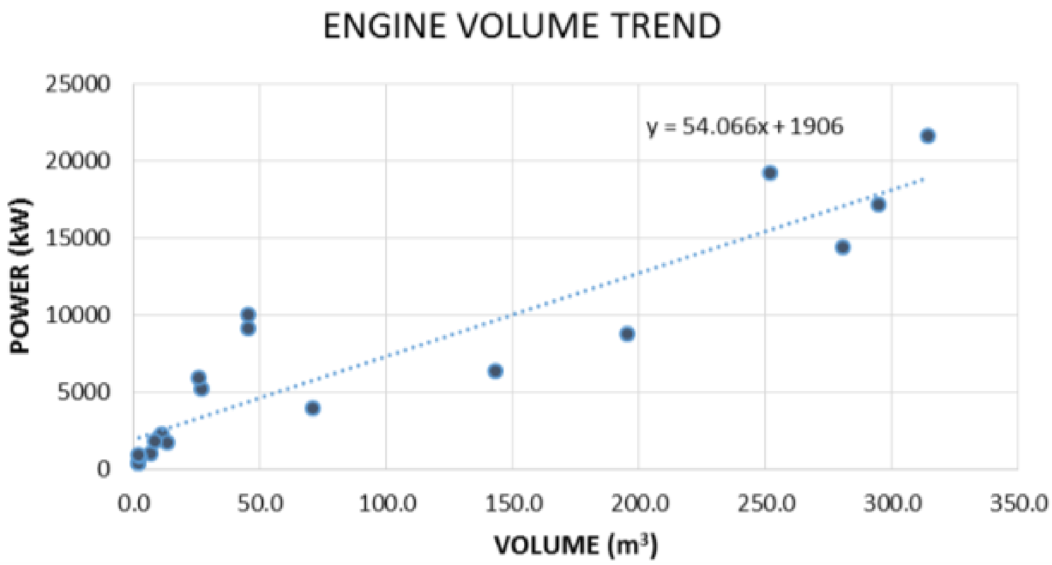

Figure 6.6: Engine volume [60]

This has so far been calculated for an internal combustion engine. If the fuel cell is taken into account, the volume of the fuel cell is calculated with the following equation.

$$\text{Power[kW]} = 55.944 \cdot \text{volume}[\text{m}^3] + 73.331 \tag{6.2}$$

The engine room contains a lot more equipment than the main engine. The engine takes up approximately 20% of the space in the engine room. The other space is there for clearances required for access and maintenance etc. With the use of a fuel cell which come in modules, the space can be better used up to 50% of the available space. The volume available for fuel cells is therefore 2.5 times higher than that of the ICE. This leaves more room for ammonia storage. The efficiency of the fuel cell is also higher at 50%. All values are shown in the table below. The maximum range the vessel can reach is 6,414 nm with the internal combustion engine and 8,050 nm with the fuel cell.

	Internal combustion engine	Fuel cell
Average cruising speed	19.6 nm/h	19.6 nm/h
Fuel margin	1.2	1.2
Efficiency	49%	50%
Main engine power	80.08 MW	80.08 MW
Density ammonia	683 kg/m^3	683 kg/m^3
Energy density ammonia	5.2 kWh/kg	5.2 kWh/kg
Volumetric density	3,527 kWh/m^3	3,527 kWh/m^3
Available space	18,198 m^3	20,328
Bunker capacity	16,920 mt or 16,752 m^3	16,920 mt or 16,752 m^3
Engine volume	1,446 m^3	3,575
Range	6,414 nm	7,311 nm

Table 6.4: Results Emma Maersk

The attainment rate is calculated by dividing the distance that the case vessels can sail on ammonia by the distance of the route researched. If the rate is greater than one, the vessel is able to sail this route on ammonia. For the vessel Emma Maersk the attainment rate is only 0,54. This is calculated with the current fuel bunkering capacity. This leads to the options of giving up cargo space or add another stop. One TEU has a volume of 38 m^3, so to be able to store enough ammonia to complete this trip in one leg, 434 container need to be replaced. This is not a large amount of a vessel that can carry 15,000 TEU. The other option is an extra stop. Along this route lies the Port of Aden in Yemen.

	ICE	Fuel cell
Range	6,414 nm	7,311 nm
Distance route	12,225 nm	12,225 nm
Attainment rate	0.52%	0,60%
Loss of cargo space	434 TEU	360 TEU
Extra stop	Port of Aden in Yemen	Port of Aden in Yemen

Table 6.5: Attainment rate Emma Maersk

Case vessels

This calculation has been done for all the case vessels. The table below shows the results. As can be seen is the attainment rate for most vessels below 1. However, with sacrificing a significant small cargo space, the vessels are able to complete the trip. The last vessel that is researched, ammonia carrier Renaud, sails a small distance of 457 nm. The attainment rate for this vessel is high. This strengthens the statement that the implementation of ammonia on short sea shipping is easier.

Vessel	**Distance travelled**	**Att. rate ICE**	**Cargo space lost ICE**	**Att. rate Fuel cell**	**Cargo space lost Fuel Cell**
Container vessels	Nm				
Emma Maersk	12,225	0.52	434 TEU	0.60	360 TEU
MSC Texas	6,604	1.08	-	1.22	-
Ever Urban	10,092	0.71	104 TEU	0.83	62 TEU
Bulk carriers					
NSU Carajas	15,302	0.28	23,314 m^3	0.3	21,992 m^3
Lowlands Blue	7,891	0.34	9,297 m^3	0.36	8,710 m^3
Darya Chand	15,241	0.31	5,634 m^3	0.34	5,229 m^{3}m^3
Ammonia carriers					
Genesis River	15,078	0,31	8,162 m^3	0.35	7,458 m^3
Yara Sela	5,215	0.78	530 m^3	0.89	251 m^3
Renaud	457	4.4	-	5.3	-

Table 6.6: Attainment rate case vessels sailing on ammonia

7
Ports

This chapter discusses the research question:

To what extent are important ports able to provide ammonia bunkering facilities?

The Initial Strategy of the IMO GHG reduction plan calls for the encouragement of port development, including ship and shore side/shore power supply from renewable sources, infrastructure for supplying alternative low-carbon and zero-carbon duels and optimisation of the logistic chain and associated planning. Many ports are already taking action to facilitate alternative options, such as shore power supply, safe and efficient bunkering of alternative fuels, incentives promoting sustainable low-carbon and zero-carbon shipping and support for optimisation of port calls. Also the cooperation between ports, bunker suppliers, shipping companies and relevant levels of authority is important to establish the supply and availability of ammonia. This also includes infrastructural barriers for efficient and safe handling and bunkering of the fuel [52].

7.1. Location and infrastructure

Around the world there are approximately 400 major bunkering ports. Most demand is located in a few strategically located ports. For the year 2012, Singapore, China, the USA, the UAE, the Netherlands and South Korea accounted for approximately 60% of the world's demand. Singapore is the biggest bunkering port by volume with annual sales of 42 million metric tonnes. This is mainly due to it being located along one of the busiest shipping lanes and close to refineries. Also the port has been known for its exceptional good infrastructure. The second largest port is Fujairah in the UAE with annual sales of 24 million mt, due to the strategic location between the shipping lanes between East and West. The third largest bunker port is Rotterdam with annual sales of 10.5 million mt, Hong Kong is fourth with 7.4 million mt and Antwerp fifth with 6.5 million mt. Other important ports are Busan in South Korea, Gibraltar, Panama, Algeciras in Spain, Los Angeles and Shanghai [13].
To be able to supply ammonia to the marine sector infrastructure and ship maintenance facilities are required. There are already 120 ports with ammonia terminals and it can therefore be assumed they have the necessary equipment and storage facilities. 38 of these ports are suited to export ammonia at this point of time and 88 ports import ammonia, 6 of which do both import and export. Many of these terminals are located at ammonia/fertiliser plants located at the coast of sea or river. Other terminals are independent of plants and have their own ammonia storage or are part of larger port complexes. [36]. Figure 6.1 shows the ammonia trade routes and quantities of August 2020. Figure 6.3 show the ports in which ammonia is transhipped. These locations can become the foundation for the network of ammonia distribution. The world maritime trade in ammonia was estimated at 17.5 million tons in 2019. This has been transported by 71 LPG tankers with cargo capacity between 2,500 and 40,000 tons. These vessel have the ability to keep ammonia at the required -34 degrees Celsius to keep ammonia liquid. Also important to take into consideration regarding vessels that do not carry ammonia as cargo is the availability of bunkering facilities in ports and impact on cargo operation time. Currently there are 120 ports in the world that can import and/or export ammonia. A solution to a quick growth in the ammonia market is ship to ship bunkering. This was also applied when LNG was introduced. It minimises investment for facilities and is very flexible. The bunkering of ammonia

simultaneously with cargo loading / unloading needs to be authorised by the Port Authorities.

7.2. Handling and transport of ammonia

Storage of ammonia comprises special isothermal tanks of up to 30,000 tons capacity and spherical pressure storage tanks between 1,000 and 2,000 tons. Special pipe and valve systems are used for filling and discharging ammonia from ships. Currently ammonia is shipped by standard semi-refrigerated and fully refrigerated gas carriers. The safety risk of ammonia is mainly in pressurised storage. If the storage leaks or when dangerous air concentration arises this can have major consequences. Ammonia is detectable at 5-50 ppm by its characteristic odour. Exposure to 700 ppm for less than an hour does not cause major injuries. To prevent spreading in case of a leak, automated ammonia gas detection and automated response systems such as alarm, increased ventilation, line shut down etc should be applied [43].
Anhydrous ammonia is a dangerous good marked as a toxic gas and must be transported according to legislation. Each year 1.5 million tons ammonia is transported by railways in Europe. Currently there are 170 ships capable of carrying ammonia, of which 40 do so continually. The ships have measures in place against leakage, firefighting procedures, procedures for cargo transfer, gas freeing, ballasting and cargo cleaning, minimum allowable cargo tank steel temperature, emergency procedures and training of personnel. The ships also have toxic vapour detection. Other safety measures include dangerous goods marking, proper maintenance of vessels, guidelines for loading and unloading, protective clothing and guidelines for emergency responses.

7.3. Policies

The Harbour Master enforces international, national and local laws and regulations in ports. The Harbour Master gives out permits, exemptions, approvals and directions for infrastructure complying with the regulations and safety policies [64]. Safety regulations for transport are already in place in other sectors. The marine industry can research these methods to incorporate safety measures in early design stages of the ships. With policies in place, harbours can adapt to the situation and invest in safe supply of ammonia to the marine sector.

Green ammonia certification

The only difference between operating green versus conventional ammonia is expected to be the purchase of a green ammonia certificate. This certificate originates from the electricity market but has made its way into more sectors. The Renewable Energy Certificate (RECs) represents MWh of electricity generated from renewable energy resource. The REC can be sold on the market as an energy commodity. The RECs are also known as Green Tag, Tradable Renewable Certificates (TRCs), Renewable Electricity Certificates or Renewable Energy Credits. This trading mechanism supports development and scale up of renewable energy, fuels and chemicals. This mechanism is expected to be implemented for green ammonia as well [43].

7.3.1. Port of Amsterdam

The port of Amsterdam is part of the five busiest harbours in West-Europe. The port had the goals to reduce GHG emissions of industry and shipping with 55% before 2030. The port is researching a number of alternative fuel options, such as electrification and hydrogen for inland shipping and methanol and ammonia for deep sea shipping. These new fuels require new infrastructure, including bunker vessels to deliver the fuel. Currently renewable fuels are more expensive than conventional fuels and shipping companies are less likely to switch to a cleaner fuel. To bridge this difference the port of Amsterdam stimulates the green energy with a pricing policy. This system uses the international measurements tool Environmental Ship Index, the ESI. In this index vessels get a discount on harbour expenses if they use technology and fuel that decreases GHG emissions. Also vessels with the Green Award, an international environment for safety and durability, get a discount [72].

7.4. Conclusion

The barriers in this section are the storage abilities including infrastructure, uncertainties in policies, fuel prices and investment costs. The transport and handling of ammonia is already in place due to shipping ammonia as a fertiliser, but bunkering is still a barrier due to loss of competitiveness and additional cost of regulations. The most important uncertainty is the fuel price. With the existing grid of ammonia terminals and storage facilities, a bunkering grid could be established fast and cost efficient by converting small gas tanker vessels to bunker barges. The existing storage facilities can be used as base stations. The bunkering is similar to other gaseous fuels, except the toxicity rather than flammability to be the greater hazard. The procedure of bunkering ammonia needs to be developed.

8

Production

This chapter discusses the next research question:

To what extent are the production locations able to supply current and future fuel demand?

As mentioned in chapter 2 ammonia is a low-climate-impact fuel if produced from either renewable energy and/or produced with carbon capture and storage (CCS). The process of production is first discussed. Then the current and logical future locations of ammonia plants is discussed, followed by an overview of all costs involved in the implementation of ammonia.

8.1. Production

Ammonia is produced with hydrogen and nitrogen. Hydrogen is produced by water electrolysis, which splits hydrogen (H_2) from water (H_2O). The electrolyser exists of either a pressurised alkaline electrolyser, a high-temperature solid oxide electrolyser or a proton exchange membrane (PEM) electrolyser. Nitrogen is separated from air, which consists for 79% of nitrogen (N_2). Air separation is an amine based absorption/desorption process. The Haber Bosch (HB) reaction is used to convert the gasses into ammonia. In this process nitrogen gas is mixed with a hydrogen gas and under the proper pressure and temperature conditions produces ammonia, shown in figure 8.1

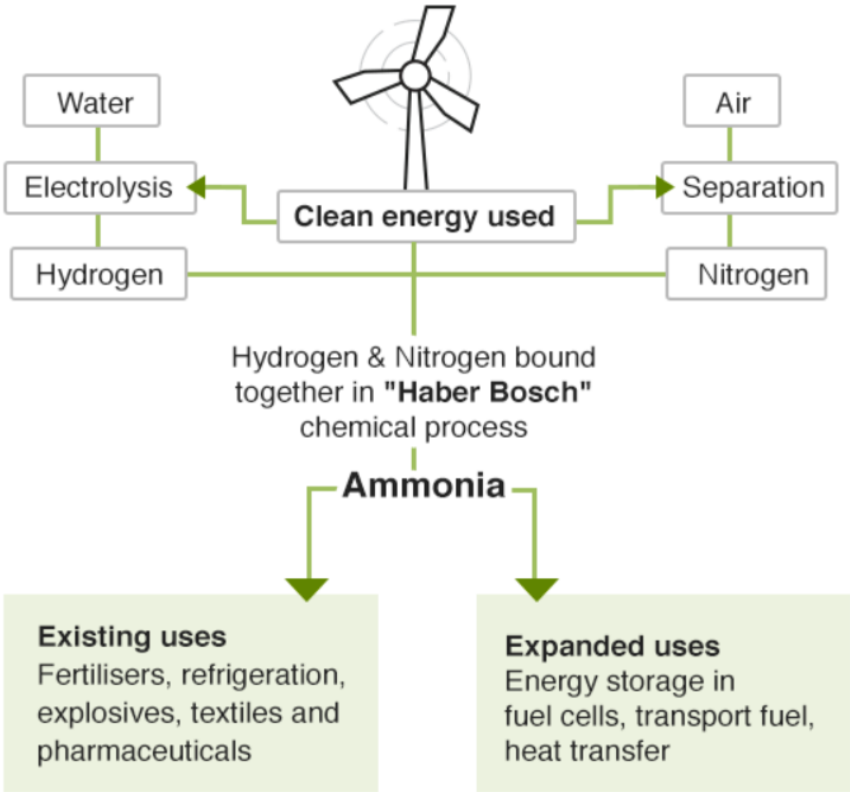

Figure 8.1: Production of green ammonia [36]

The HB process needs 53 kWh of electricity to generate 1 kg of hydrogen. Based on the higher heating value of hydrogen (142 MJ/kg) this corresponds to an average efficiency of 74.5% and based on the lower heating value of hydrogen of 120 MJ/kg an efficiency of 63%. During production 10-12 kWh per kg NH_3 is needed [43][30]. The ammonia synthesis reaction is run under pressures between 7 and 30 MPa and temperatures between 400 and 500 °C. Grinberg et al. [32] assumes that in the future the hydrogen needed in the production will be sourced by water separation. The overall production of ammonia is then given in the following formula. In this reaction all hydrogen from the feedstock is used, so ammonia has a 100% hydrogen utilisation efficiency due to the use of the HB process. Two mole ammonia is produced with one mole N_2. The minimum energy needed to separate N_2 from air is about 60 MJ/t. This results in 220 MJ for cryogenic air separation.

$$\begin{aligned} N_{2(g)} + 3H_2O_{(l)} \rightarrow 2NH_{3(g)} + 1.5O_{2(g)} \\ \delta H^o_{Rxn} = +382.8kJ/mol \end{aligned} \tag{8.1}$$

8.1.1. Water Electrolysis

There are currently three promising technologies to produce hydrogen by electrolysis, namely Alkaline Electrolysis (AE), Proton Exchange Membrane Electrolysis (PEM) and Solid Oxide Electrolysis Cells (SOEC). The main technology is AE and is being scaled up. The largest AE plant lies in Malaysia and produces 25 MW at 5500 Nm_3/h.

The PEM electrolysers are based on a polymer membrane electrolyte and precious metal electrodes. This is an advantage over AE that used potassium hydroxide solution which needs to be recovered and recycled. The PEM achieve better current densities which allows for more compact water electrolysis units. Other advantages are the very fast response time of milliseconds and the dynamic load range of zero to above 100% in capacity. Challenges with the PEM include the production cost due to the precious metal and the lower energy efficiencies. This technology is also used for local hydrogen production in the fuel cell, discussed in section 5.2.2.

SOEC is the least developed technology so far and isn't yet scaled up or commercialised. This technology

operates at a high temperature of 700-800 °C and therefore has an energy efficiency advantage over the other technologies. Part of the energy needed to produce hydrogen can be supplied by the high temperature heat and when integrated with heat generation chemical reaction the overall energy efficiency is attractive. Also the cost potential appears to be lower as well.
The AE energy efficiency is 63% currently and is expected to increase to 65% or even 70% in the long term. PEM is expected to reach similar energy efficiencies and had the best potential in fast electrical load changes. This technology is however more expensive due to the precious metal content. SOEC's also are expected to reach similar price levels and have the potential of 90% overall energy efficiency when integrated with ammonia synthesis. Conventional ammonia has a footprint of 2 tons CO_2 per ton ammonia made from natural gas and 3 tons CO_2 produced with coal. Blue ammonia has the same numbers, but the CO_2 is captured and stored. Green ammonia has an assumed footprint of zero. This does ignore the full life-cycle-analysis which includes the plant construction and transport of ammonia. The estimation of life cycle emission reduction for wind power-based green ammonia is >90% and >75% for photovoltaic (conversion of light into electricity) based ammonia [43].

In the case the marine industry has an ammonia fuel demand of 30% in 2030 150 million tons/year should be produced just of the marine industry, taking the lower energy density into consideration. This requires 400 GW in total. The current electrolysis and synthesis technology requires 10 MWh/tNH_3, so 1500 TWh. The energy efficiency of power-to-ammonia is however expected to increase by up to 20% over the next decade [43].

Produced ammonia has one of three colour references; viz. green, blue or brown (also called black or conventional ammonia). Ammonia has the reference colour green when the hydrogen is produced with sustainable energy such as biomass, renewable electricity, nuclear and solar energy. Blue ammonia is made when the process is fuelled by hydrocarbons and/or carbon capture and storage (CCS). In this process hydrogen is produced by using methane reforming (SMR). 90% of the CO_2 produced is from this process [76]. The CO_2 is captured rather than emitted into the atmosphere. This process is however quite costly and energy intensive [3]. Brown, or conventional, ammonia is made with fossil fuel and is currently the majority of ammonia produced. The current production process creates massive GHG emissions, around 1.8% of the global CO_2 emissions and consumes around 2% of the world's energy [36][76][75].

The Institute for Sustainable Process Technology (ISPT) has started a project to form hydrogen by water electrolysis powered by solar and wind energy for the production of green ammonia [33]. At the time of writing ammonia however is still mainly produced with fossil fuel-based hydrogen. The production with renewable energy sources is still in development [35]. It is believed that new large scale green ammonia production plants will operate with this process because it is efficient and can produce lowest cost ammonia if supplied continuously with renewable electrical energy. To achieve a higher efficiency rate is it therefore better to use continuous supplies of electric energy, such as hydro-electricity or geothermal electricity rather than weather dependent solar, wind, wave or tidal energy [3].

The HB process to make green ammonia costs between 1.9 and 2.9 m€/MW. This process is not yet ready to be used on a large scale. First the HB process needs to be up-scaled and developed for higher production capacities. Then the first plant needs to be build in order to gain experience. The next step is development of a new reactor for process intensification and improvements in reaction kinetics, energy efficiency and decrease in capital costs. Finally, the development of new catalysts will create a more durable and cost-effective process [30]. This process is still in the early stages. The technology is developed and most components are available. The only component that is not ready is the HB reactor. To be able to achieve high enough production rates, multiple reactors will have to run in parallel.
Research is still been done on the correct process variables regarding reactor pressure, inert gas percentage in synthesis loop, NH_3 concentration, H_2-to-N_2 ratio, total flow rate and feed temperature. Inert gas fraction and H_2-to-N_2 ratio have very high flexibility, namely 255% operational flexibility for Ar, up to 51 to 67% flexibility for hydrogen intake and 73% reduction and 24% enhancement in ammonia production. The system is viable for power-to-ammonia process within a set range. Outside this range the reactor system shuts down due to overheating the catalyst. [18]. Producing with the HB process is only cost-effective when produces on massive scale due to high energy demand and expensive materials that are required. In the current method produces more CO_2 than any other chemical-making reaction. The current way consumes 2% of world's

energy demand and produces 1% of its CO_2. Also the majority of ammonia is now produced in centralised location, consuming more energy to transport around the globe [63] .

8.1.2. Current production

Ammonia (NH_3) is produced in large quantities all over the world [88]. The current production levels are however named differently in different studies. One study says the current production of ammonia is 180 million tonnes per year [43]. A consortium of companies [43] however states that the current production is capable of 243 million tons and has an over capacity of roughly 60 million tons/year. Table 8.2 shows the production of ammonia per region. This should produce enough fuel to support the initial demand for marine propulsion. This could serve as an introduction with stable costs and availability, however still with brown ammonia. The consortium names ammonia to be a strategic fuel in a transition phase with switching from fossil-fuel based ammonia to green ammonia. This transition should lower the CO_2 emission and the risk for the ship owner gradually [43].
The current main ammonia type is brown ammonia and 80% of the production is used for fertiliser production, such as urea, ammonium nitrate and ammonium phosphate. If the marine industry will adapt ammonia as a fuel, it will compete with the food production [35]. Another downside is that the production of brown ammonia has no significant reduction of CO_2 emissions. This leads to a need for production of blue and green ammonia [11].
In other reports the ammonia production on 2018 has been stated at 230 million tons/year and in 2019 at 235 million tons/year. This report expects the production to be roughly 290 million tons/year in 2030. This forecast entails the capacity growth of 107 planned and announced ammonia plants, primarily located in Asia and the Middle East. The plants are expected to be up and running in 2030.

Region	**2018/19**
	(1000 metric tons Ammonia)
North America	19.477
Latin America	13.644
Western Europe	12.214
Central Europe	8.341
Eurasia	31.033
Africa	12.828
West Asia	22.247
South Asia	22.426
East Asia	98.819
Oceania	2.259
World Total	**243.288**

Figure 8.2: Production of ammonia per region [43]

8.1.3. Future production

Since the production numbers differ quite a bit, the lower and higher number are both taken into consideration for the calculations of future fuel demand. Table 8.1 shows an overview of the numbers in four scenarios. All scenarios have a yearly required ammonia production of 150 million tons by 2030. The first scenario is the lower number of 180 million tons and assumes no overcapacity at the moment. In this scenario the full 150 million tons need to be added to production. The second scenarios is assuming a current production level of 243 million tons, which is in overcapacity of 63 million tons. The further 87 million tons need to added to production. The third scenario assumes the production will be 290 million tons by 2030 by the planned new-builds of production plant. This would require only 40 million tons more in production. In the fourth scenario Ammonfuel[43] believes the 150 million tons/year will be realised by 2050 by conversing an existing plants and building new plants. This scenario is the only longer term scenario. 25% of the ammonia synthesis capacity can be obtained from conversing ammonia plants with available technology within compressor and reactor technology. This should increase the current availability of 243 million tons to 304 million tons world capacity per year. Table 8.1 shows the production levels of the low and high estimation of the current levels, as well as the 2030 forecast and the conversing estimation.

Scenario	**1**	**2**	**3**	**4**
Current	180	243	290	304
Required	150	150	150	150
Overcapacity	0	63	110	124
Needed	150	87	40	26

Table 8.1: Production levels ammonia in million tons

Green ammonia

The path from conventional to green ammonia is technically feasible and should be done by converting existing plants into hybrid plants. Initially, in these hybrid plants green ammonia has the lowest possible cost, compared to an all green ammonia production plant. With this initial production of green ammonia, the industry can adapt and the demand for green ammonia grows. This then leads to more demand for green production plants.

The hybrid plants can easily produce 10% green ammonia with very little expenditure. Going over the 10% green electricity supply in a hybrid ammonia plant will require modifications in the heat integration, which requires further investments. New plants that are built as hybrid plant can produce 25% green ammonia with capacities more than twice as much as conventional plants. Hybrid plants are ideal in areas with high penetration of renewable power production plants. Renewable energy can then be produced at low cost and high capacity factor. The plant produces green ammonia in periods of high wind and solar production and traditional ammonia in low periods. The bottleneck for hybrid production plants to scale up the green ammonia production is the production capacity of electrolysers. This level is currently quite low since the demand is low. By converting existing plants the addition of electrolysers is gradual. The demand rises and so the production would too of this well-proven technology with no scaling barriers. Due to the current lack of electrolysers the first green ammonia plants will be only of 100 MW. Figure 8.3 shows the projected ammonia production in the next 30 years of the conservative level.

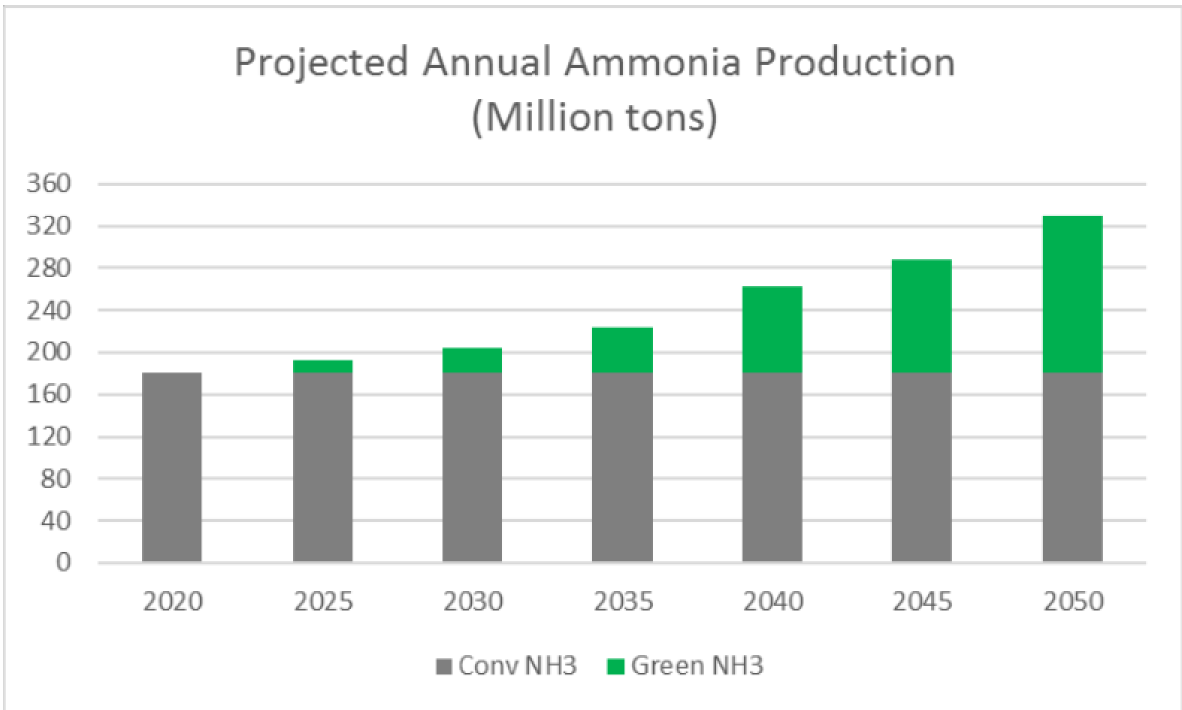

Figure 8.3: Projected annual ammonia production [43]

The pathway to green ammonia is given in the next table 8.4.

Initial phase 2020-2030	Scale-up phase 2025-2035	Green commercial phase 2035-2050
• Conventional ammonia amply available worldwide for ammonia fueled ships • Allows competitive solution to meet sulfur requirements in shipping • No CO2 emission from the ship due to ammonia driven propulsion • Certified blue ammonia (central carbon capture) and hybrid revamp green ammonia (renewable energy) increasingly available at moderately higher cost	• Continued growth of certified blue ammonia and hybrid revamp green ammonia • First dedicated green ammonia plants followed by initial scale up in size and number of plants • Learning curve for electrolysis, green ammonia and power-to-X technologies in general drives down cost of green ammonia • Lowering life-cycle CO2 emissions from shipping with increasing percentage of green ammonia	• Emerging and later multiplication of large scale green ammonia plants in regions of low cost and high capacity factor renewable energy • >150 million tons / year of green ammonia available for the shipping industry • Green ammonia contributes 30% or more to total shipping fuel need towards the end of the period enabling fulfillment of IMO GHG emission goals

Figure 8.4: Pathway to green ammonia [43]

8.1.4. Electrical power

One of the biggest challenges in producing green ammonia is the electricity supply. Where electricity was earlier supplied by a stable power grid, the new renewable energy source option from wind and solar power plants have major fluctuations. The concern is whether the production plant can handle these fluctuations in the supply. Haldor Topsøe A/S, a leading catalyst supplier in the ammonia industry, have designed a system that can handle these fluctuations. This system has a turn-down ratio of 10-100% with a constant synthesis pressure without power or hydrogen storage. With a storage the turn-down ratio of 0-100% is feasible. Another system that Haldor Topsøe A/S has been working on is the solid oxide electrolysis cell (SOEC). This system will improve efficiency for electrolysis with a 30% specific energy consumption improvement compared to conventional ammonia plants and alkine electrolysis. Figure 8.5 shows the difference between production between SOFC and SOEC. The SOC performs as an oxygen separation membrane, ammonia cracker and heat exchanger. This technology is however still in a low TRL and will not be commercially available in the coming years [71].

In 2019 184 GW in additional power production was installed. The total installed capacity up until 2020 is 650 GW in wind power and 636 GW in solar power. The annual grow rates of renewable power is about 20-30%. To be able to produce this amount of ammonia between 2020 and 2040 200 GW in additional power should be installed, which is a very manageable task. [43].

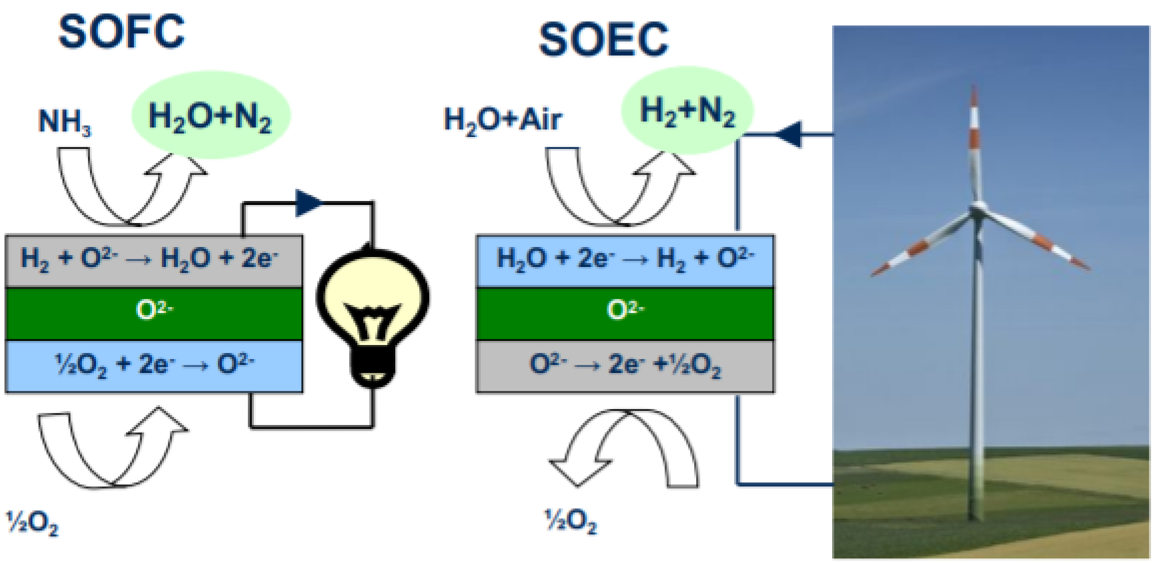

Figure 8.5: chemical reaction in SOFC and SOEC [71]

8.2. Location and transportation

While looking into feasible and logical production locations for ammonia, a few things are important. The first one is the availability of area to build a production plant to meet the demand for green ammonia. The challenge here lies in the availability of land with good wind and solar resources. On a good wind site 1 GW of turbines required 100 km^2. A solar photovoltaics (PV) plant would cover only 20 km^2 for 1 GW, which could be located between the wind turbines. Figure 8.6 shows the area required for wind energy to supply 30% of global marine fuel consumption. Currently, there are several initiatives looking into the production of renewable ammonia. The producer Yara is planning a demonstration plant with solar energy in Australia [35]. Australia is also a fine example for use of wind energy and Iceland has large geo-thermal and wind energy [3]. Secondly, the production location should preferably lie close to an ammonia supplying port. During transportation additional gasses are emitted which are included in the total emission count of ammonia. It is therefore important to locate production plant on strategic locations to minimise emissions in the supply chain.

Figure 8.6: Area required to produce 30% of global marine fuel demand with wind power [43]

8.2.1. Current locations

The current ammonia production is connected with natural gas, so the plants are located where natural gas is extracted; Russia, Middle East and North Africa. Another logical location is the United States, where plenty natural gas is available. Also India has many ammonia plants, despite the scarce natural gas sources but India imports much LNG, to become self-sufficient in fertiliser supply. In 2018 new ammonia plants were built in USA and Indonesia. Demand for ammonia is mostly expected in China, India and Morocco [25]. These production plants all lie close to large ammonia ports and are therefore strategically located. The next figure show the biggest ammonia import and export countries in 2017.

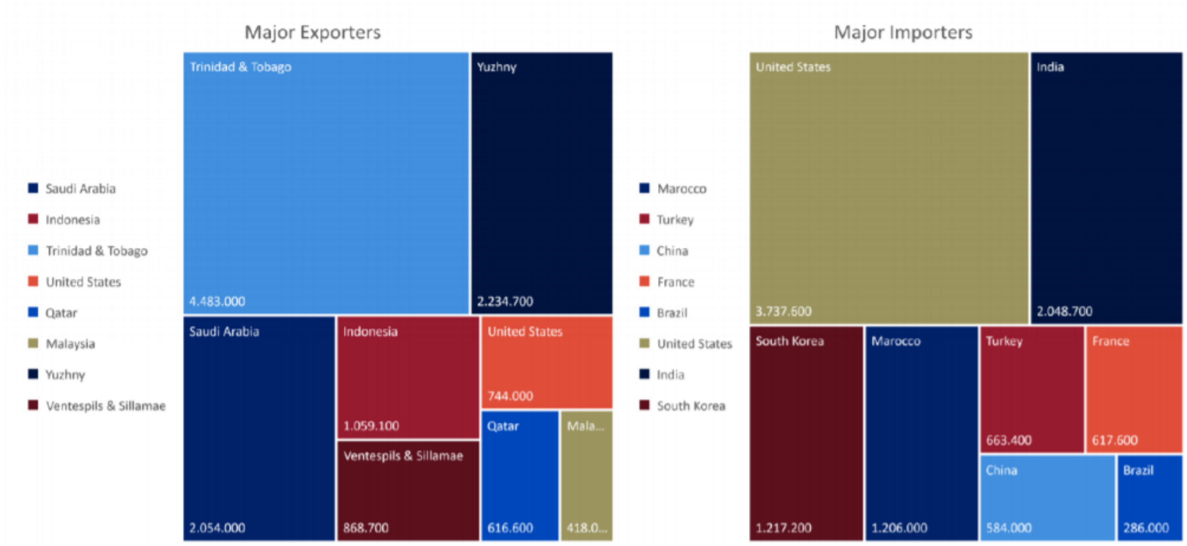

Figure 8.7: Ammonia import and export in 2017 [25]

Recently Maersk and DFDS announced a new project in Denmark, viz.to build Europe's largest Power-to-X-facility to produce green ammonia. The plant will use offshore wind turbines to supply 1 GW of electric power for electrolysis [17].

8.3. Fuel price and costs

At the time of writing this report the price indications from different parties are quite different. A consortium of companies named Ammonfuel [43] states that the cost of green ammonia will be similar to compliant fuel and that current ammonia fuel is already comparable. Sangberg et al. [71] agrees with this statement saying that the cost of brown ammonia (developed with the use of natural gas) costs currently 250 USD/mt. Blue ammonia (developed with natural gas with carbon capture and storage technology, minimising carbon emissions by 2/3) costs currently between 350 and 400 USD/mt. Green ammonia (produced by front-end electrolysis in existing ammonia plants) costs also between 350 and 400 USD/mt, but the price is expected to drop to 250 USD/mt in the future. MAN ES also expects ammonia to match the price of LPG, LNG and methanol [36]. Buitendijk et al. [11] says the average price of ammonia of approximately 300 USD/mt is similar to the VLSFO price. However, the price of green ammonia is at the moment 2 to 3 times higher than of brown ammonia made of natural gas, but is similar to the price of brown ammonia made from coal.
As expected there are at the moment no OPEX benefits of switching to ammonia compared to conventional fuel and there is an increasing CAPEX. Switching to ammonia is at the moment not beneficial, but is believed to be so in the future when the price of renewable electricity decreases [11].
De Vries [24] however names very different prices in 2019. A ton of ammonia amounted to 1030 USD and a ton low sulphur 0.5% HFO to about 600 USD. This leads to believe that the earlier named prices are too optimistic. Ammonfuel [43] has made the following estimation of fuel costs of USD/ton; 650-850 in 2025, 400-600 in 2030. The price per ton does not seem to differ too much from the VLSFO price, but due to the lower energy density ratio, the price per GJ is higher than VLSFO. Between 2040 and 2050 it is however expected that green ammonia has the same price. Table 8.2 shows an overview of the above discussed numbers and able 8.8 shows the calculations of the consortium Ammonfuel. The costs are discussed in more detail in the sections below.

	Sangberg	Buitendijk	De Vries	Ammonfuel
Brown ammonia	250	300, similar to VLSFO	1030 stated HFO at 600	250
Blue ammonia	350-400	-	-	350 - 400 in 2025-2030 350 - 400 in 2040-2050
Green ammonia	350 - 400 250 in future	600 - 900 from nat gas 300 from coal	-	650 - 850 in 2025 400 - 600 in 2030 275 - 450 in 2040-2050
Hybrid green ammonia	-	-	-	300 - 400 in 2025-2030 250 in 2040-2050

Table 8.2: Ammonia prices estimations in USD/mt

	2025-2030		**2040-2050**	
Assumed renewable electricity price	30EUR/MWh		20EUR/MWh	
	Price Per ton USD/MT	Price per GJ LHV USD/GJ	Price Per ton USD/MT	Price per GJ LHV USD/GJ
VLSFO (<0.5%S)	500-600**	12.5-15	500-600**	12.5-15
Conventional ammonia	250**	13.5	250**	13.5
Blue ammonia	350-400	18.8-21.5	350-400	18.8-21.5
Green ammonia	400-850*	21.5-45.7	275-450	14.8-24.1
Hybrid Green ammonia	300-400***	16.1-21.5	250	13.5

Figure 8.8: Market prices estimation for different classes of ammonia [43]

Conventional ammonia

The price of conventional ammonia is build up of fixed operating costs including storage costs, cost of energy and potential CO_2 emission penalty cost. The CAPEX cost is considered a sunk cost (already made) due to the surplus in ammonia production. The fixed operating cost ranges between 40-70 USD/mt and is dependable on plant size and location. Smaller plants and high cost areas are more expensive. The cost of energy is the largest contribution with 75-85%. The specific energy consumption is approximately 8.4 MWh/mt given an energy cost of 70-200 USD/mt and an natural gas price of 70-200 USD/m^3. The already existing ammonia plants have a 20% higher energy consumption. The future CO_2 penalty cost is expected to be between 25-75 USD/t CO_2. A typical plant produces 2 tons CO_2 per ton NH_3, so the penalty lies between 50-150 USD/mt NH_3.

Blue ammonia

Blue ammonia costs are build up by cost of the conventional ammonia without CO_2 penalty, cost of CO_2 capture from flue gasses (0.8 T_{CO_2}/T_{NH_3}) and cost of CO_2 liquefaction, short-term storage, transport and long term storage (2 T_{CO_2}/T_{NH_3}). For a natural gas plant the CO_2 production and emission is from: 1) approximately 1.2 ton CO_2 per ton NH_3 (T_{CO_2}/T_{NH_3}) that is obtained as a pure CO_2 stream from the separation process of ammonia synthesis feed and 2) between 0.4 to >1 T_{CO_2}/T_{NH_3} that is emitted in low concentrations in flue gas from heat generating combustion processes. This is 1.2 T_{CO_2}/T_{NH_3} of pure CO_2 and 0.8 T_{CO_2}/T_{NH_3} in flue gas (exhaust gases exiting to the atmosphere).

The total cost Capex and Opex of carbon capture of 0.8 is estimated to be 60 USD/T_{CO_2}, which amounts to 50 USD/t_{NH_3}. The remaining cost of CO_2 liquefaction, transport and storage lies between 25 and 50 USD/T_{CO_2} for all 2 T_{CO_2}/t_{NH_3}, which comes to 50 - 100 USD/T_{NH_3}. Figure 8.9 shows the estimated prices of blue ammonia and conventional ammonia.

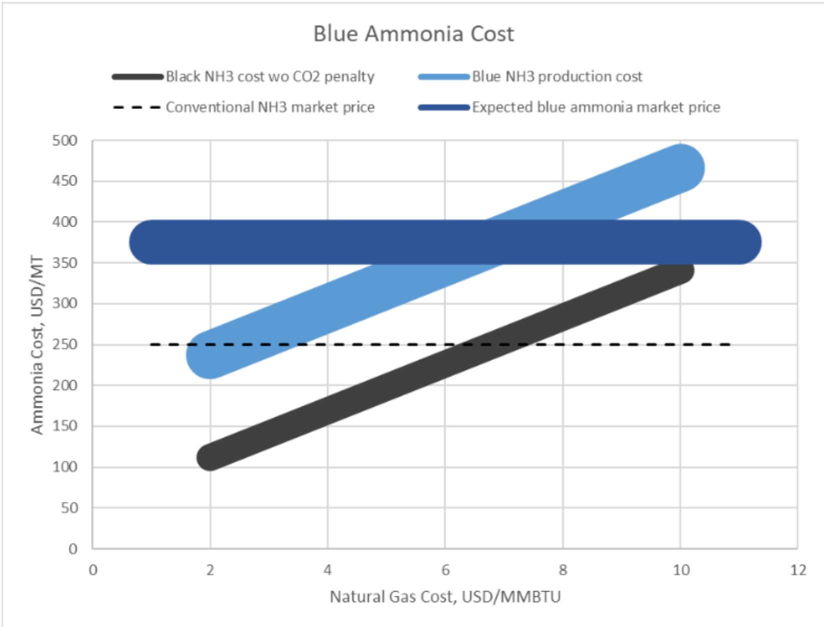

Figure 8.9: Estimated production cost and market price of conventional and blue ammonia [43]

Green ammonia

As mentioned in 8.1.3 it is believed that with conversion of production locations into green production plants the goal of 30% of the global fleet sailing on green ammonia by 2050 could be met. However, to meet this goal a significant investment needs to be done. This raises the questions how much investment is needed to meet this goal and what determines whether or not this investment is made?

For the production costs the process consists of water electrolysis, electrically driven air separation and the traditional Haber-Bosch synthesis. The plant up-time is expected to 96% and the capacity factor 85% of the 7150 full load hours per year. While scaling up a production plant, the core of the electrolysis unit will scale linearly with the plant size. Other installation costs will drop with increasing plant size. The total sum of capital investment cost and fixed operating cost will range between 375-475 USD/mt for a 100 MW plant size and 190 USD/mt for a 1 GW plant size on the 2025-2030 time scale. These estimates take Alkaline, PEM and SOEC electrolysis in consideration. For 2040 the learning curve is expected to reduce the cost between 150-190 USD/mt. The total energy consumption will be 10-10.5 MWh/mt for alkaline and PEM or 7.6-7.8 MWh/mt for SOEC. The price for renewable electricity in 2025-2030 will probably be around 36 USD/MWh. The learning curve is expected to reduce this price to 24 USD/mt by 2040. Figure 8.10 shows the expected production cost of green ammonia in relation with changing electricity costs.

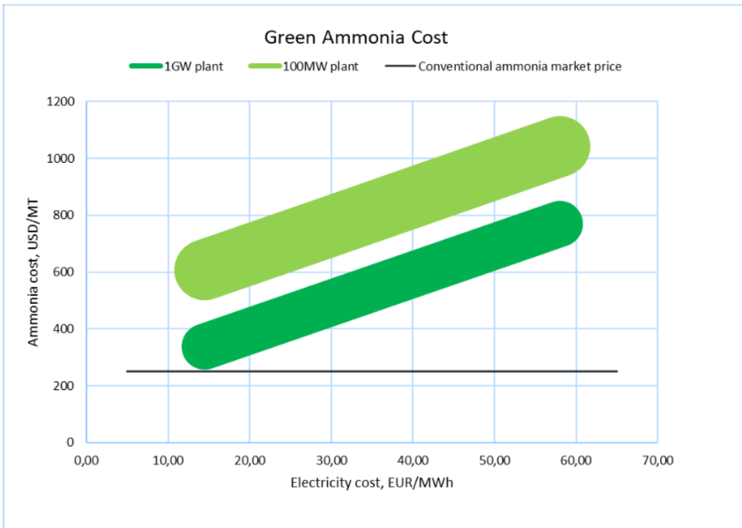

Figure 8.10: Estimated production cost of green ammonia [43]

Hybrid green ammonia
As mentioned before the switch to green ammonia will likely be with hybrid green ammonia as a step in between. In this process an existing ammonia synthesis plant is used and an electrolysis front end is added next to the natural gas front end. The cost of hybrid green ammonia is build up of; additional conversion CAPEX and fixed operating costs + additional cost of electricity - cost of saved natural gas - saved CO_2 penalty. The only significant cost modification is the electrolyser installation. The production process remains the same, but 10% of the hydrogen feed is from the electrolyser. With this a saving of 13-16% of total consumed natural gas is reached. The relative amount of green ammonia in the produced mix is stated as the total CO_2 savings. This plant has great benefits in using existing ammonia plant scale and assets.
Conversion of existing plants will decrease the cost of ammonia significantly. With a new plant to produce ammonia the specific capital cost lies around 666 USD/ton. With conversion of a plant and adding 20% additional capacity, the cost drops to 300 USD/ton [20]. The additional total sum of capital expenditure cost and fixed operating cost is estimated to be between 80-130 USD/mt. The specific additional electricity consumption is estimated 6-9 MWh/mt of green ammonia produced. The price in 2025-2030 for hybrid green ammonia is expected to be 300-400 USD/mt. From 2040 onward this is expected to drop to 250 USD/mt, the present market price of conventional ammonia. The break-even green ammonia sale price is almost independent of the natural gas price.

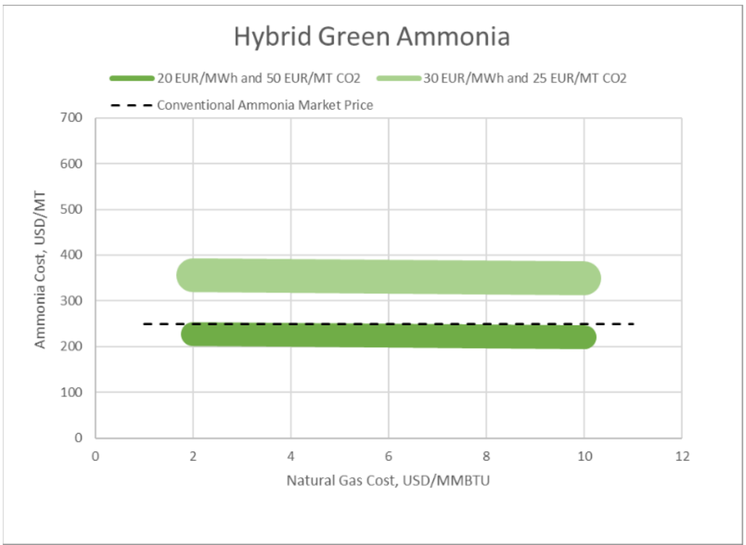

Figure 8.11: Break even price of hybrid green ammonia [43]

Fuel price competitor fuels The price of ammonia will always be higher than conventional fuels. If ammonia is implemented in the marine industry is dependent on the fuel price of other alternative fuels. The gap between these fuels, including ammonia, and conventional fuel can be closed by subsidies to make the switch to alternative fuels more attractive. The prices for the other fuel options are for methanol priced between 430 and 519 USD/mt [19], for LNG between 176 and 193 USD/mt [1] and for green hydrogen is the price currently 625 USD/mt.

8.3.1. Investment costs

Hendrik Brinks, Principal researcher of DNV GL- Maritime states that in order to be able to produce enough ammonia for the shipping industry a 4.5 trillion USD investment is required. The main cost of production of green and blue ammonia stems from the electrolysis process. The electricity production will absorb about 3.2 trillion USD (with wind power) and 1.3 trillion USD is needed for the ammonia plants. This concerns only the production itself, since the network of supplying ammonia to the ports is already in place with current ammonia use [11]. This however is based on the whole global fleet sailing on green ammonia. That is not a realistic scenario. To produce enough ammonia for the world fleet a facility of 300 km^2 is required to produce enough green ammonia (650 million tonnes). This production requires as much as the whole Chinese electricity production, namely 6,500 TWh [11]. This is based on the lowest current ammonia production level. As mentioned before is green ammonia in the hybrid plant the lowest possible cost option. The first 10% of green ammonia is easily produced, but a higher percentage requires investments for modifications. Producing in higher volumes is then also more cost efficient than on larger scale. The numbers mentioned by Hendrik Brinks can therefore not be linear adapted to lower production volumes.

To make a clear indication of investment costs two examples are used, one of a smaller plant conversion and one of a larger plant newly build. The first one is PJSC Dorogobuzh which is part of the Acron Group. This plant has been upgraded to produce ammonia more efficiently and with a reduction of 7%/t natural gas consumption. The capacity went from 1,740 tpd to 2,100 tpd with an investment of 67,8 million USD. The production volume per year went up by 130,000 tons [15].
The second example is Gulf Coast Ammonia LLC, Air Products and Eastman Chemical Company. This plant is expected to be running in 2023 in Texas and produce roughly 1.3 million tons ammonia per year, which is 9% of the world supply. The investment for this location is 600 million USD in construction, operation and ownership. 500 million USD is invested towards infrastructure to get utilities to the plant and transport hydrogen through pipelines, large steam methane reformer to produce hydrogen and the construction of an air separation unit to supply nitrogen [14]. Adapting the two cases for the volume listed in section 8.1.3, the following investment costs come to light.

Production level ammonia	**conversion plant**	**New build plant**
150	78,231	126,923
87	45,374	73,615
40	20,862	33,846
26	13,560	22,000

Table 8.3: Investment costs in million USD for conversion versus new build

In comparison the scale up of hydrogen is estimated at 150 billion USD needed by 2030. The cost of hydrogen is then 15 USD/MMBtu (2 USD/kg) by 2030 and is even expected to fall to 7.4 USD/MMBtu (1 USD/kg) by 2050. This makes hydrogen competitive with the current natural gas prices in China, India, Brazil and Germany. Cost could be 20-25% lower in countries with best renewable and hydrogen storage resources, such as in the U.S., Brazil, Australia, Scandinavia and the Middle East. The cost however would be up 50-70% in Japan and Korea where there are weaker renewable resources and unfavourable geology for storage. Also an abatement of 1/3 of global emissions from fossil fuels and industries and a reduction of up to 20% of global emissions for under 100 USD/tCO_2 when using 7.4 USD/MMBtu hydrogen is expected. However, the scaling up is not yet put in motion due to lack in policy support [8].
Bloomberg NEF [8] expects hydrogen to take up 7% of the world's energy needs by 2050 with 187 million metric tons with moderate policies in place where global warming is limited to 1.5 degrees. With strong policies 696 million metric tons is expected to be produced, taking up 24% of the world's energy demand. This requires an investment of 11 trillion USD in production, storage and transport infrastructure. The annual sales

are expected to be 700 billion USD. To be able to produce 24% of energy demand 31,320 TWh is needed to power the electrolysers. That is more than currently is produced worldwide. The cost of an alkaline electrolyser has fallen 40% between 2014 and 2019 made in North America and Europe and 80% in China. If the alkaline electrolyser is scaled up and costs continue to fall, renewable hydrogen is expected to be produced for 0.7 to 1.6 USD/kg by 2050. This is equivalent to gas priced at 6-12 USD/MMBtu [8].

9
Results

This chapter looks back at the barriers and the mutual interactions and relationship stated in table 4.1 and the insights gathered in this thesis.

Vessel implementation

To be able to sail on ammonia, a suitable power system needs to be available and operable. The first obstacle in this aspect is the availability of a power system. The current engines are not able to burn ammonia as a fuel. The first ICE is expected to be operable in 2024. This a dual-fuel engine from MAN. Due to it being a dual-fuel engine, the risk of designing a power system for one type of fuel is reduced. While the regulations are not yet set in place, the engine can run on another fuel. The engine can run on both liquid and gas fuel. The engine does have a higher upfront cost, but it is expected to be beneficial in the long run. The goal of 2024 is for an ICE for large scale container ships. Later on the company wants to release a retrofit package for existing vessels. Challenges in the engine are:

- Ammonia is toxic and potentially corrosive –> Complete system design form fuel tank to engine. System includes double walls.
- Preventing nitrous oxide (N_2O) to be emitted

This thesis looked into the implementation of ammonia on board of three types of vessels, namely; container vessels, bulk carriers and ammonia carriers. This is because they sail on fixed routes, make up the majority of the world fleet in gross tonnage and will therefore have the largest fuel consumption. They sail on fixed routes between two ports, so less ports to supply ammonia are needed, the ammonia carriers already carry the fuel so comply with the regulations, they sail over large distances (larger fuel consumption, larger demand). The vessels in the scope often sail on a slow-speed two-stroke ICE. Ammonia carriers already carry the toxic fuel on board. The problem is that when it is used as a fuel, the fuel gets closer to the people on board. Rules need to be implemented for this scenario.

Fuel cell is the most efficient way of using ammonia, but does not deliver enough power to drive an ocean going tanker. Ammonia needs to be split into hydrogen, nitrogen and water first. A barrier in this system is that the conventional membrane, the proton exchange membrane which is used in hydrogen fuel cells, is not suitable for ammonia. The hydroxide exchange membrane fuel cell (HEMFC) is suitable. This fuel cell has a lower efficiency than the hydrogen fuel cell, due to ammonia being more difficult to oxidise than hydrogen. PEMFC can only use hydrogen so ammonia needs to be cracked and purified first. An alkaline fuel cell also only runs on hydrogen but the ammonia doesn't need to be purified first. The SOFC can use ammonia directly. The SOFC is slow due to its thermal response properties and the start-up time is several hours. These fuel cells are not yet commercially available but have only been used in lab experiments and in tests on ships. The barriers on this fuel cell are the power density and the load response capabilities. Also the total cost of ownership is higher than the ICE option and the savings on the OPEX take too long to be beneficial. The final option is the AmmoniaDrive. This is a hybrid ICE-SOFC power system that has a 5 -8 % higher power-generation efficiency compared to the conventional set-up. The SOFC produces hydrogen that is fed to the

ICE. A selective catalytic reduction (SCR) system is added to reduce NO_x and NH_3 from the exhaust gasses. This is a relatively large engine compared to the SOFCs, which are a realistic power plant configuration regarding space and weight requirements, capital expenditure (CAPEX) and transient capabilities.

Storage
The second barrier is onboard storage facilities. There are some systems required for storing ammonia on board. These systems require special design requirements, which are dependent on the next barrier, the regulations.

Regulations The third barrier is the regulations that ships using ammonia as a fuel have to comply with. Without rules in place shipping companies face a large risk of implementing a system that later on might not be suitable according to the rules. This will hold back companies to make the switch to ammonia. This then will delay the process of implementing the rules because the demand for ammonia is not high enough for the governing bodies to accept this as an urgent matter and take legislation in hand. This reciprocity can delay the whole process.
Additionally, the process of getting the regulations in writing is very long. To be able to make an estimate of the time path of getting new rules in place in addition to the existing IGF code, the example of methanol is used. Even if the IMO puts this topic on the agenda for the next meeting, it will be around late 2024 when the regulations are in place. The first step in this process is however not taken yet, so it will most likely be later than that, meaning that the engine will become commercially available before the regulations are in place.
The main reason for not starting to implement ammonia related rules is the lack of demand from the marine industry. The demand, however, is dependent on whether or not ammonia is allowed to be used and what design requirements the rules entail.
Another barrier is the risk assessment of the safe handling of ammonia. As stated in 5.5 the technology needed is already in use for LNG, which has a comparable process. The only extra evaluation should be on the lower flammability and the toxicity of ammonia. Since ammonia is already being shipped is it reasonable to assume that ammonia will comply with the rules.
Finally, the costs are a barrier. The use of an ICE with ammonia is expected to be 3.2 times as expensive as the conventional option. This can however change in the future if the price of ammonia gets more competitive and the use of conventional fuel comes with a taxation for CO_2 emissions. The fuel cells have a higher CAPEX, so the ICE is the more obvious choice for shipping companies. Also other systems required for storing and using ammonia as a fuel have a direct impact on the CAPEX and OPEX.

Routing

The vessels in the scope of this thesis are chosen because they often sail on a fixed route. When the vessels switch to ammonia, the range of the vessel could be affected. Ammonia has a lower energy density than conventional fuel, but a higher energy density than most alternative fuels. If the vessels aren't able to reach the route in one leg, the option is either to add another stop or to give up cargo space to be able to carry more fuel. Especially deep sea sailing doesn't always have the option for an extra stop, so they are more likely to have to give up some cargo space.

Availability of ammonia for vessels

Whether or not shipping companies will switch to ammonia is also dependent on the availability of ammonia in ports. Fortunately the infrastructure for transporting ammonia through ports is already available due to ammonia being used as fertiliser and is transported globally.
The second barrier is the storage abilities in the ports. This includes infrastructure and storage itself as well as investment costs. The ports on the most common routes have ammonia storage facilities available. Many of these terminals are located at ammonia/fertiliser plants located at the coast of sea or river. Other terminals are independent of plants and have their own ammonia storage or are part of larger port complexes.
Another barrier in the port aspect is the bunker facilities in the port as well as bunker time. The bunker time can be cut down by ship-to-ship or barge-to-ship bunkering. This also minimises investment in facilities and is very flexible. Also with bunkering ship-to-ship only offshore regulations are applicable and not local regulations. This could be an advantage in some locations. The barrier in this process are the port regulations. This is very location dependent if and when this will be allowed.
The final barrier in this section is uncertainties in regard to policies in specific ports. The cooperation be-

tween ports, bunker suppliers, shipping companies and relevant Governmental bodies is important to establish the supply and availability of ammonia. This also has a bearing on infrastructural barriers for efficient and safe handling and bunkering of the fuel.

Production capacity

The current process of producing brown and blue ammonia consumes 2% of the global energy demand and causes 1% of global CO_2 emissions. The production process needs to switch to green and/or hybrid ammonia to reduce emissions in production. The first barrier in this aspect is the unavailability of the entire process. Production capacity's bottleneck for green ammonia is the scale-up (production capacity) of the electrolysers in the Haber Bosch reactor. The only cost-effective way is to produce ammonia on a large scale, since it requires large amounts of energy and expensive materials. This is not yet feasible and will need investment to convert or build new production plants.
The current production capacity is not enough to fuel a significant part of the global fleet in order to meet the Paris Agreement. To reach that goal, at least 30% should be sailing on ammonia by 2030. Global production capacity needs to be increased.
The fact that the Haber-Bosch reactor is not yet commercially available does however not impact on the implementation of ammonia. Conventional ammonia can first be used before a gradual switch to green ammonia is made. It is not a bottleneck in the whole logistical chain.

Alternative fuel options

The mutual interaction and relation depicted in figure 4.1 and the barriers between them discussed in table 4.1 are now more clear. However, to be able to say if ammonia will be implemented in the marine industry, the relation between the aspects of other alternative fuels should be made. These critical success factors can than be compared to each other to determine which fuel has the higher probability of implementation in the marine sector. The demand for an alternative fuel is highly dependable of the other options and the ship owners will likely choose the cheapest option. Once an alternative fuel is used in a significant part of the market, the other alternative fuels are very unlikely to be implemented. This is a great risk of ammonia since the availability is expected to be in 2030 while methanol is expected in 2025 and bio-LNG is easy to implement for vessels that already sail on LNG.

10
Conclusions

The current policy measures sparks low ambition to meet the IMO GHG strategy. Mechanisms to stimulate the investment in costly technology, such as subsidies, should be made and promoted by public and private actors. Examples of this are the Norwegian NO_x fund and the Green Shipping programme. These supportive procurement policies and long term contracts promoting low-carbon and zero carbon shipping could also help the change to alternative fuel despite the costly technology and therefore investment. The fuel mix in 2050 will depend heavily on regulations and the cost of the fuel converter systems and fuel itself. Unless the alternative fuels become price competitive with fossil fuels, policy measures are needed to address GHG emissions directives.

Changing to a less competitive fuel will impact on costs, asset values and earning capacity. Ship owners are therefore not likely to change to an alternative fuel on their own. This greatly impacts on the choice of fuels and technology. For the sake of good order it is noted that the technical readiness level of other alternative fuels is higher, with the inherent change and risk that ship owners will choose for one of these alternative fuels and will not change to ammonia when this has matured sufficiently for use on board. The ship owner will always choose the cheaper options.

DNV GL looked into both the point of view of policy makers and that of the industry itself that want to decarbonise the world fleet. The other stake holders are the ship owners that have to make a short-term decision with long-term implications. The future is quite uncertain and is mainly dependent on economic development, future energy policies, human behaviour and reaction to policies and pricing trends. The policies needed are requirements for individual ships and policy measures to support desired development and implementation of new technology. It is not expected that alternative fuels will be economically competitive with traditional fuels within the next few years. With supportive policy a large-scale production and establishment to reach availability and reasonable pricing can be made possible. Approximately 70% of the sailing fleet in 2050 will have been built after 2030. To prevent extensive retrofit of engines and fuel systems the policies should be ready by 2030 [28].

Bibliography

[1] Energy Information Administration. Natural gas, 2021. URL https://www.eia.gov/dnav/ng/hist/n9133us3M.htm.

[2] Maritime Studies South Africe. Types of bulk carriers, 2020. URL https://maritimesa.org/grade-10/types-of-bulk-carriers/.

[3] Ammoniaman. Green and Blue Ammonia, 2019. URL https://ammoniaman.com.au/2019/01/09/green-and-blue-ammonia/.

[4] G Bas, K. De Boo, A.M. Vaes-Van de Hulsbeek, and I. Nikolic. MarPEM: An agent-based model to explore the effects of policy instruments on the transition of the maritime fuel system away from HFO. *Transportation Research Part D: Transport and Environment*, (55):162–174, 2017. doi: 10.1016/J.TRD.2017.06.017.

[5] Duurzaam Bedrijfsleven. Ammoniak als brandstof in oceaantanker, 2020. URL https://www.duurzaambedrijfsleven.nl/logistiek/33167/ammoniak-brandstof-scheepvaart.

[6] Yusuf Bicer and Ibrahim Dincer. Clean fuel options with hydrogen for sea transportation: A life cycle approach. *International Journal of Hydrogen Energy*, 43(2):1179–1193, 2018. ISSN 03603199. doi: 10.1016/j.ijhydene.2017.10.157. URL https://doi.org/10.1016/j.ijhydene.2017.10.157.

[7] Black and Veatch. Ammonia: Fuel vs. hydrogen carrier, 2021. URL https://www.bv.com/perspectives/ammonia-fuel-vs-hydrogen-carrier.

[8] BloombergNEF. Hydrogen Economy Outlook. Technical report, 2020. URL https://data.bloomberglp.com/professional/sites/24/BNEF-Hydrogen-Economy-Outlook-Key-Messages-30-Mar-2020.pdf.

[9] T. Brahim, F. Wiese, and M. Münster. Pathways to climate-neutral shipping : A Danish case study. *Energy*, 188:116009, 2019. ISSN 0360-5442. doi: 10.1016/j.energy.2019.116009. URL https://doi.org/10.1016/j.energy.2019.116009.

[10] R.A. Broome, M.E. Cope, B. Goldsworthy, L. Goldsworthy, K. Emmerson, E. Jegasothy, and G.G. Morgan. The mortality effect of ship-related fine particulate matter in the Sydney greater metropolitan region of NSW, Australia. *Environmental International*, 87(-):85–93, 2016.

[11] M Buitendijk. 'producing enough green ammonia for shipping requires a usd 4.5 trillion investment', 2020. URL https://www.swzmaritime.nl/news/2020/10/23/producing-enough-green-ammonia-for-shipping-requires-a-usd-4-5-trillion-investment/.

[12] M. Buitendijk. Waterfront shipping: 'methanol as a marine fuel works', 2020. URL https://www.swzmaritime.nl/news/2020/03/10/waterfront-shipping-methanol-as-a-marine-fuel-works/.

[13] Ship bunker news team. 6 countries are responsible for almost 6-% of all bunker sales, 2016. URL https://shipandbunker.com/news/world/608701-6-countries-are-responsible-for-almost-60-of-all-bunker-sales.

[14] businessfacilities. $1b ammonia plant coming to greater houston, 2020. URL https://businessfacilities.com/2020/01/1b-ammonia-plant-coming-to-greater-houston/.

[15] J. Casey. Dorogobuzh invests over rub 5 billion in ammonia plant upgrades, 2020. URL https://www.worldfertilizer.com/project-news/05082020/dorogobuzh-invests-over-rub-5-billion-in-ammonia-plant-upgrades/.

[16] Rentar Fuel Catalyst. How efficient are engines: Thermodynamics and combustion efficiency, 2018. URL https://rentar.com/efficient-engines-thermodynamics-combustion-efficiency/.

[17] S. Chambers. Maersk invests in danish green ammonia production plant, 2021. URL https://splash247.com/maersk-invests-in-danish-green-ammonia-production-plant/.

[18] I.I. Cheema and U. Krewer. Operating envelope of Haber–Bosch process design for power-to-ammonia. Technical report, 2018. URL https://pubs.rsc.org/en/content/articlehtml/2018/ra/c8ra06821f.

[19] Chemanalyst. Methanol prices overview, 2021. URL https://www.chemanalyst.com/Pricing-data/methanol-1.

[20] ChemicalEngineering. Chemical process plants: Plan for revamps, 2015. URL https://www.chemengonline.com/chemical-process-plants-plan-revamps/.

[21] European Commission. Eu emissions trading system (eu ets), 2020. URL https://ec.europa.eu/clima/policies/ets_en.

[22] European commission. Cleaner air in 2020: 0.5% sulphur cap for ships enters into force worldwide, 2020. URL https://ec.europa.eu/commission/presscorner/detail/en/IP_19_6837.

[23] P. De Vos. AmmoniaDrive: a solution for zero-emission shipping?! . *SWZ Maritime*, (141):36–37, 2020.

[24] N. De Vries. Safe and effective application of ammonia as a marine fuel. Technical report, Delft University of Technology, 2019.

[25] G. Dimopoulos. Ammonia as a marine fuel: marine engineering, safety and regulatory considerations, 2019. URL http://www.smartcats.eu/wp-content/uploads/2019/05/SMARCATS_DNVGL_Dimopoulos_14042019-release.pdf.

[26] T. Do. Imo 2020 and effects on the shipping industry, 2019. URL https://www.seahawk-investments.com/2019/08/28/imo-2020-and-effects-on-the-shipping-industry-2/?lang=en.

[27] E4tech. Master plan for CO2-reduction in the Dutch shipping sector – Biofuels for Shipping. (May), 2018. URL www.platformduurzamebiobrandstoffen.nl.

[28] O. Endresen, M.S. Eide, and Longva T. Maritime forecast to 2050. 2019.

[29] ETIP. Marine biofuels. *ETIP Bioenergy*, 2018.

[30] European Association for Storage and Energy. Power to ammonia - gasoline synthesis from h2 and n2 by using water electrolysis and air separation, 2018. URL https://ease-storage.eu/wp-content/uploads/2018/09/2018.08_TVAC_WG1_TD-Power-to-Ammonia.pdf.

[31] C. Gable and S. Gable. What Is Compression Ignition?, 2019. URL https://www.thoughtco.com/what-is-compression-ignition-85351.

[32] issn = 15213773 journal = Angewandte Chemie - International Edition keywords = alternative fuels,chemical hydrogen storage,energy conversion,nitrogen,nitrogen-based fuels number = 31 pages = 8798–8805 title = Nitrogen-Based Fuels: A Power-to-Fuel-to-Power Analysis volume = 55 year = 2016 Grinberg Dana, A. and Elishav, O. and Bardow, A. and Shter, G.E. and Grader, G.S., doi = 10.1002/anie.201510618.

[33] Groenervaren. Is ammoniak de brandstof van de toekomst? URL https://www.groenervaren.nl/is-ammoniak-de-brandstof-van-de-toekomst/.

[34] R.A. Halim, L. Kirstein, O. Merk, and L.M. Martinez. Decarbonization Pathways for International Maritime Transport : A Model-Based Policy Impact Assessment. 2018. doi: 10.3390/su10072243.

[35] J. Hansson, S. Brynolf, E. Fridell, and M. (2020) Lehtveer. The potential role of ammonia as marine fuel-based on energy systems modeling and multi-criteria decision analysis. *Sustainability (Switzerland)*, 12 (8):10–14, 2020. ISSN 20711050. doi: 10.3390/SU12083265.

[36] R. Harrabin. Climate change: Fertiliser could be used to power ocean-going ships, 2020. URL https://www.bbc.com/news/business-51548361.

[37] E Herben, R.S. Laursen, N. De Vries, and A. Valera-Medina. Ammonia as marine fuel, 2018. URL https://nh3fuelassociation.org/wp-content/uploads/2018/11/AEA-Imp-Con-01Nov18-Session-4.pdf.

[38] EU SCIENCE HUB. Renewable energy – recast to 2030 (red ii), 2019. URL https://ec.europa.eu/jrc/en/jec/renewable-energy-recast-2030-red-ii.

[39] The Maritime Safety Committee International Maritime Organization. New code of safety for ships using gases or other low flashpoint fuels (igf code) agreed in draft form by imo sub-committee, 2014. URL https://www.imo.org/en/MediaCentre/PressBriefings/Pages/28-CCC1IGF.aspx.

[40] The Maritime Safety Committee International Maritime Organization. Maritime safety committee, 102nd session (msc 102), 4-11 november 2020 (virtual session), 2020. URL https://www.imo.org/en/MediaCentre/MeetingSummaries/Pages/MSC-102nd-session.aspx.

[41] ITF. International code of safety fpr ships using gases or other low-flahspoint fuels (IGF code). Technical report. URL https://www.itfglobal.org/sites/default/files/node/resources/files/ITF%20Guideline%20on%20IGF%20Code.pdf.

[42] M. Krijgsman. De maritieme energietransitie begint met de binnenvaart. *SWZ Maritime*, 1(2):28–31, 2019.

[43] Alfa Laval, Hafnia, Haldor Topsoe, Vestas, and Siemens Gamesa. Ammonfuel – an industrial view of ammonia as a marine fuel. August:1–59, 2020.

[44] Shipping law news. Air pollution in shipping: The further reduction of so2 emissions 2020, 2019. URL https://www.hellenicshippingnews.com/air-pollution-in-shipping-the-further-reduction-of-s02-emissions-2020/.

[45] D.S. Lee. Update of Maritime Greenhouse Gas Emission Projections. Technical report, 2017. URL www.ce.nl.

[46] C Lhuillier, P Brequigny, F. Contino, and C Rousselle. Performance and Emissions of an Ammonia-Fueled SI Engine with Hydrogen Enrichment. *SAE Technical Paper*, 24:11, 2019. ISSN 0148-7191. doi: https://doi.org/10.4271/2019-24-0137.

[47] X. Mao, D. Rutherford, L. Osipova, and B Comer. Refueling assessment of a zero-emission container corridor between China and the United States: Could hydrogen replace fossil fuels? Technical report, 2020. URL www.theicct.org.

[48] The maritime executive. Opec forecasts falling hfo prices and more scrubber orders, 2018. URL https://maritime-executive.com/article/opec-forecasts-falling-hfo-prices-and-more-scrubber-orders.

[49] International maritime organization (IMO). Energy efficiency measures, -. URL http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Technical-and-Operational-Measures.aspx.

[50] International maritime organization (IMO). Eedi - rational, safe and effective, 2012. URL http://www.imo.org/en/MediaCentre/HotTopics/GHG/Pages/EEDI.aspx.

[51] International maritime organization (IMO). Third IMO GHG Study 2014, 2014. URL http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Greenhouse-Gas-Studies-2014.aspx.

[52] International maritime organization (IMO). Invitation to member states to encourage voluntary cooperation between the port and shipping sectors to contribute to reducing GHG emissions from ships. Technical report, 2019. URL http://www.imo.org/en/OurWork/Environment/PollutionPrevention/Documents/Resolultion%20323%2874%29.pdf.

[53] International maritime organization (IMO). Energy efficiency measures, 2020. URL http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Technical-and-Operational-Measures.aspx.

[54] International maritime organization (IMO). Greenhouse gas emissions, 2020. URL http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/GHG-Emissions.aspx.

[55] International maritime organization (IMO). Prevention of air pollution from ships, 2020. URL http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Air-Pollution.aspx.

[56] International maritime organization (IMO). Nitrogen oxides (nox) – regulation 13, 2020. URL http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Nitrogen-oxides-(NOx)-%E2%80%93-Regulation-13.aspx.

[57] International maritime organization (IMO). Sulphur oxides (sox) and particulate matter (pm) – regulation 14, 2020. URL http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-(SOx)-%E2%80%93-Regulation-14.aspx.

[58] International maritime organization (IMO). Introduction to imo, 2020. URL http://www.imo.org/en/About/Pages/Default.aspx.

[59] Methanex. About methanol, 2020. URL https://www.methanex.com/about-methanol/methanol-marine-fuel.

[60] J.J Minnehan and J.W. Pratt. Practical Application Limits of Fuel Cells and Batteries for Zero Emission Vessels. Technical report, Sandia National Laboratories, 2017.

[61] B. Mishra. Shipping industry and the nox emissions, 2019. URL https://seanews.co.uk/features/shipping-industry-and-the-nox-emissions/.

[62] D. Nelissen and Huigen T. De feiten op een rij. Technical report, 2017. URL www.ce.nl.

[63] University of New South Wales. New eco-friendly way to make ammonia could be boon for agriculture, hydrogen economy, 2021. URL https://www.sciencedaily.com/releases/2021/01/210121091332.html.

[64] Port of Rotterdam. Legislation and regulations. URL https://www.portofrotterdam.com/en/shipping/legislation-and-regulations.

[65] European Union official website. 2020 climate energy package, -. URL https://ec.europa.eu/clima/policies/strategies/2020.

[66] European Union official website. 2030 climate energy framework, -. URL https://ec.europa.eu/clima/policies/strategies/2030.

[67] European Union official website. 2050 long-term strategy, -. URL https://ec.europa.eu/clima/policies/strategies/2050.

[68] European Union official website. Fuel quality, -. URL https://ec.europa.eu/clima/policies/transport/fuel_en.

[69] Opensea.pro. An overview of the types and sizes of dry cargo and tanker ships, 2021. URL https://opensea.pro/blog/ships-types-and-sizes.

[70] J. Ren and H. Liang. Measuring the sustainability of marine fuels: A fuzzy group multi-criteria decision making approach. *Transportation Research Part D: Transport and Environment*, 54(54):12–29, 2017.

[71] B. Sangberg, P. Han, and P. Kirkeby. Is the shipping industry ready for ammonia?, 2020. URL https://marine-offshore.bureauveritas.com/magazine/shipping-industry-ready-ammonia.

[72] T. Schröder. De toekomst van de scheepvaart: nieuwe brandstoffen vragen om transitie in de haven, 2020. URL https://www.duurzaambedrijfsleven.nl/logistiek/35033/schone-scheepvaart?q=%2Flogistiek%2F35033%2Fschone-scheepvaart&utm_source=nieuwsbrief&utm_medium=e-mail&utm_campaign=Weekly+Updates+12+November.

[73] M. Seijlhouwer. Energielabel voor grote schepen moet sector duurzamer maken, 2020. URL https://www.duurzaambedrijfsleven.nl/logistiek/35143/scheepvaart-energielabel-co2?q=%2Flogistiek%2F35143%2Fscheepvaart-energielabel-co2&utm_source=nieuwsbrief&utm_medium=e-mail&utm_campaign=Daily+Focus+24+November.

[74] H Selin. Global warming, 2020. URL https://www.britannica.com/science/global-warming.

[75] R.F. Service. Ammonia—a renewable fuel made from sun, air, and water—could power the globe without carbon, 2018. URL https://www.sciencemag.org/news/2018/07/ammonia-renewable-fuel-made-sun-air-and-water-could-power-globe-without-carbon#.

[76] The Royal Society. Ammonia: zero-carbon fertiliser, fuel and energy store, 2020. URL https://royalsociety.org/topics-policy/projects/low-carbon-energy-programme/green-ammonia/.

[77] K. Soeteman. Is ammoniak de brandstof van de toekomst? URL https://www.channelweb.nl/artikel/achtergrond/technologie/6782749/6208290/brandstofcellen-op-ammoniak-is-geen-toekomstmuziek.html.

[78] J. Spoelstra. Ammoniak als scheepsbrandstof, 2017. URL https://www.maritiemnederland.com/nieuws/ammoniak-als-scheepsbrandstof.

[79] J. Stewart. Ammonia for fuel cells, 2019. URL https://www.udel.edu/udaily/2019/august/yushan-yan-direct-ammonia-fuel-cells/.

[80] M Stopford. *Maritime Economics 3rd edition.* 2009. ISBN 0-203-89174-0. doi: 9780415275576. URL https://docs.google.com/file/d/0B8MtLHcYnWCGZU8zbnB0cVN2VlE/preview.

[81] Electronic Quality Shipping Information System. The 2019 World Fleet Report Statistics from Equasis. Technical report, Electronic Quality Shipping Information System, 2020.

[82] GPF Team. Top container ship trade routes, 2020. URL https://geopoliticalfutures.com/top-container-ship-trade-routes/.

[83] Toolshero. Critical success factors, -. URL https://www.toolshero.com/strategy/critical-success-factors/.

[84] C. Trimmer and J. Godar. Calculating maritime shipping emissions per traded commodity, 2019. URL https://www.sei.org/publications/shipping-emissions-per-commodity/.

[85] R. Verbeek, P. 't Hart, J. Pruyn, and J. Bergsma. Final Report: Assessment of alternative fuels for seagoing vessels using Heavy Fuel Oil. Technical report, Netherlands Maritime Land and Ministry of Economic Affairs, 2020.

[86] L. Vogelzang. Alternative Fuels for Short Sea Shipping in Europe. Technical report, Delft University of Technology, 2019.

[87] C.L Volger. Alternative fuels on board of carbon-neutral cruise vessels. page 122, 2019.

[88] Rijksinstituut voor Volksgezondheid en milieu. Stikstof - Ammoniak (NH), 2019. URL https://www.rivm.nl/stikstof/ammoniak.

[89] Z. Wan, M. Zhu, S. Chen, and D. Sperling. Pollution: Three steps to a green shipping industry, 2016. URL https://www.nature.com/news/pollution-three-steps-to-a-green-shipping-industry-1.19369.

[90] Wolfstreet. The engines of the largest container ships in the world, and challenges their manufacturers face, 2018. URL https://wolfstreet.com/2018/05/28/the-engines-of-the-largest-container-ships-in-the-world-and-challenges-their-manufacturers-f

[91] J. Yliskylä-Peuralahti. Sustainable Energy Transitions in Maritime Transport: The Case of Biofuels. *The Journal of Sustainable Mobility*, 3(2):67–93, 2017. doi: 10.9774/gleaf.2350.2016.de.00005.

A

Overview world fleet

Figure A.1: Overview of world fleet in 2015 [62]

					2015 CO_2-emissies per schip per jaar (kt)		
Scheepstype	**Scheepsgrootteklasse**		**Aantal schepen 2015**	**CO_2-emissies 2015 (Mt)**	**Volledig op LNG varend**	**Gemiddeld 2015 emissies**	**Volledig op HFO varend**
Bulk carrier	0-9.999	dwt	1.305	5,7	3,2	4,4	4,4
Bulk carrier	10.000-34.999		2.415	24,6	7,4	10,2	10,3
Bulk carrier	35.000-59.999		3.256	45,6	10,2	14,0	14,1
Bulk carrier	60.000-99.999		2.422	46,0	13,8	19,0	19,1
Bulk carrier	100.000-199.999		1.381	38,1	20,0	27,6	27,8
Bulk carrier	200.000-+		316	11,0	25,2	34,8	35,1
Chemical tanker	0-4.999	dwt	1.511	5,2	2,5	3,4	3,5
Chemical tanker	5.000-9.999		929	6,8	5,3	7,3	7,4
Chemical tanker	10.000-19.999		1.046	11,8	8,1	11,2	11,3
Chemical tanker	20.000-+		1.481	28,7	14,1	19,4	19,5
Container	0-999	TEU	1.116	12,2	7,9	10,9	11,0
Container	1.000-1.999		1.279	29,0	16,4	22,7	22,8
Container	2.000-2.999		723	24,1	24,2	33,4	33,7
Container	3.000-4.999		920	48,8	38,4	53,0	53,5
Container	5.000-7.999		570	40,7	51,8	71,4	72,0
Container	8.000-11.999		345	29,1	61,1	84,2	84,9
Container	12.000-14.500		124	10,0	58,5	80,7	81,4
Container	14.500-+		23	2,1	68,4	94,3	95,0
General cargo	0-4.999	dwt	11.655	22,9	1,4	2,0	2,0
General cargo	5.000-9.999		2.929	16,2	4,0	5,5	5,6
General cargo	10.000-+		1.977	27,0	9,9	13,7	13,8
Liquefied gas tanker	0-49.999	m^3	1.038	10,4	7,2	10,0	10,1
Liquefied gas tanker	50.000-199.999		485	31,3	46,8	64,5	65,0
Liquefied gas tanker	200.000-+		44	4,9	80,7	111,3	112,2
Oil tanker	0-4.999	dwt	3.491	14,4	3,0	4,1	4,1
Oil tanker	5.000-9.999		668	4,4	4,7	6,5	6,6
Oil tanker	10.000-19.999		190	2,1	7,9	10,9	10,9
Oil tanker	20.000-59.999		657	12,3	13,6	18,7	18,9
Oil tanker	60.000-79.999		394	9,5	17,5	24,1	24,3
Oil tanker	80.000-119.999		922	24,6	19,4	26,7	26,9

					2015 CO_2-emissies per schip per jaar (kt)		
Scheepstype	Scheepsgrootteklasse		Aantal schepen 2015	CO_2-emissies 2015 (Mt)	Volledig op LNG varend	Gemiddeld 2015 emissies	Volledig op HFO varend
Oil tanker	120.000-199.999		477	16,5	25,1	34,6	34,9
Oil tanker	200.000-+		608	34,8	41,5	57,2	57,7
Other liquids tankers	0-+	dwt	149	1,0	4,7	6,4	6,5
Ferry-pax only	0-1.999	GT	3.068	10,4	2,5	3,4	3,4
Ferry-pax only	2.000-+		71	1,0	10,6	14,7	14,8
Cruise	0-1.999	GT	198	1,1	3,8	5,3	5,3
Cruise	2.000-9.999		69	0,6	5,9	8,1	8,2
Cruise	10.000-59.999		114	6,8	43,1	59,4	59,9
Cruise	60.000-99.999		87	15,0	125,2	172,6	174,0
Cruise	100.000-+		51	10,6	151,3	208,6	210,3
Ferry-RoPax	0-1.999	GT	1.662	4,2	1,8	2,5	2,5
Ferry-RoPax	2.000-+		1.194	26,0	15,8	21,7	21,9
Refrigerated bulk	0-1.999	dwt	1.296	20,3	11,3	15,6	15,8
Ro-Ro	0-4.999	GT	1.573	17,9	8,3	11,4	11,5
Ro-Ro	5.000-+		490	15,5	23,0	31,7	32,0
Vehicle	0-+	# voertuigen	330	7,1	15,7	21,7	21,9
Vehicle	4.000-+		660	21,1	23,2	32,0	32,3
Yacht	0-+	GT	1.561	3,4	1,6	2,2	2,2
Service – tug	0-+		14.610	20,6	1,0	1,4	1,4
Miscellaneous – fishing	0-+		22.229	49,6	1,6	2,2	2,2
Offshore	0-+		6.871	26,7	2,8	3,9	3,9
Service – other	0-+		580	11,7	14,6	20,2	20,3
Miscellaneous – other	0-+		5.801	7,2	0,9	1,2	1,2
			109.357	**928**			

B

Import and export ports ammonia

Figure B.1: Terminals in Asia and Oceania

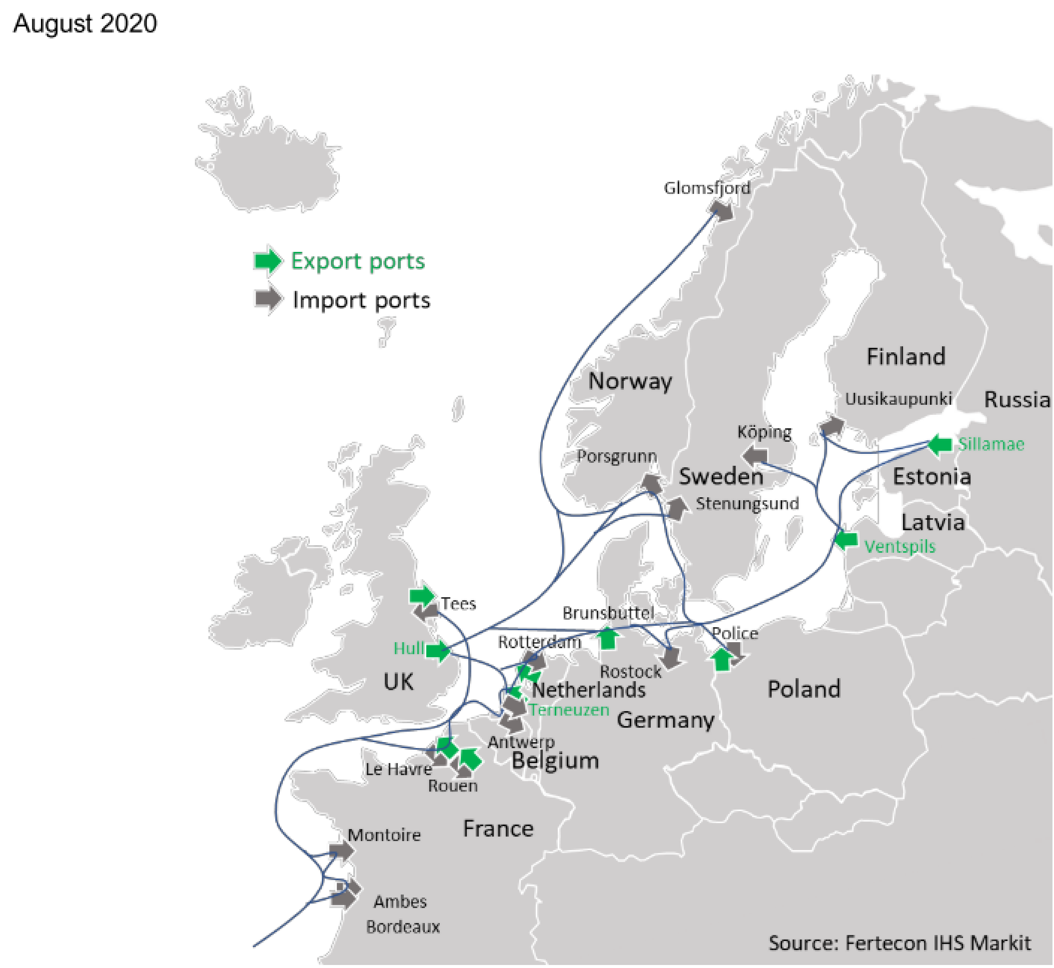

Figure B.2: Terminals in Baltic

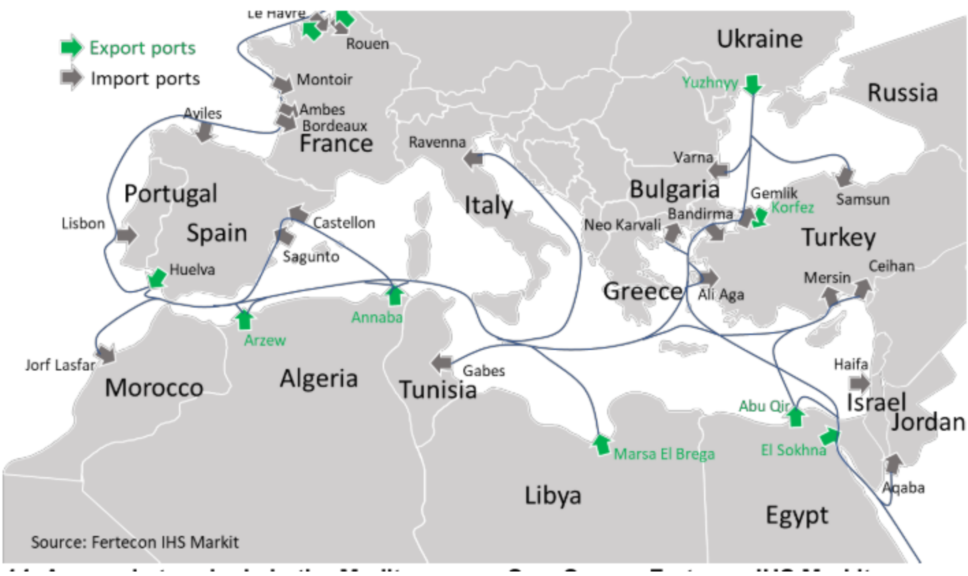

Figure B.3: Terminals in Mediterranean

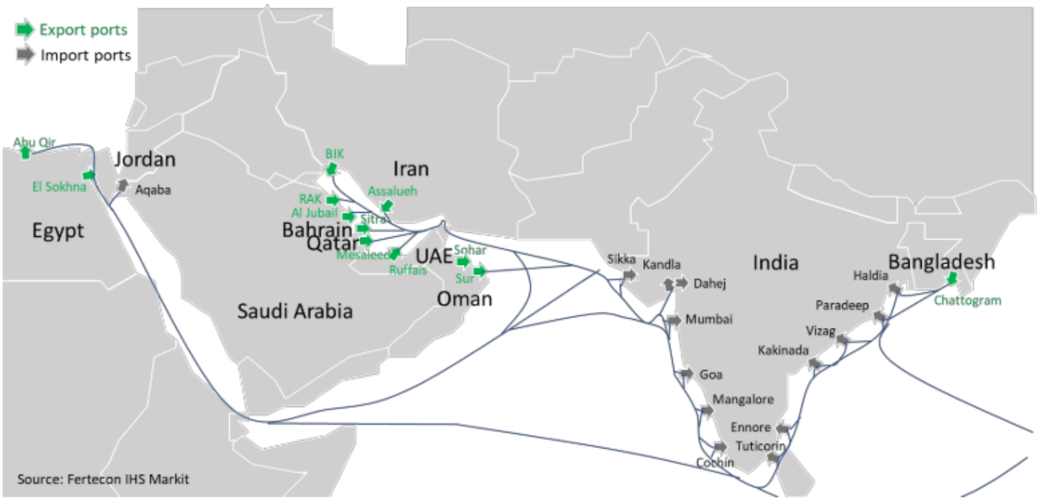

Figure B.4: Terminals in Middel East

Figure B.5: Terminals in South America

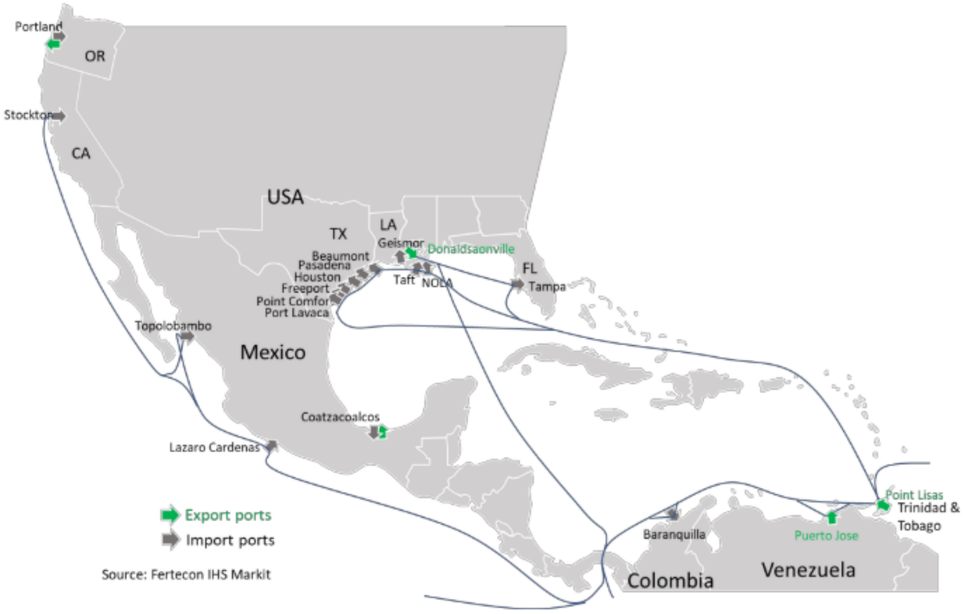

Figure B.6: Terminals in North America and Caribbean