

Andrea Rygh Steinsvik
Eirun Hagen Birkeland
Kristine Marie Embretsen

Production and usage of blue ammonia in maritime transport

Produksjon og bruk av blå ammoniakk i maritim transport

Bachelor's thesis in Engineering, Renewable Energy
Supervisor: Pauline Zimmermann
May 2023



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Science and Technology

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*Eirun Birkeland**Andrea Steinsvik**Kristine M. Embretsen*

Preface

This thesis serves as the final assignment for the bachelor's program: Bachelor in Engineering, Renewable Energy, under the Department of Energy and Process Engineering at the Norwegian University of Science and Technology (NTNU).

PhD Candidate Pauline Zimmermann was the internal supervisor of this thesis. We are sincerely grateful for her valuable help, insight and expertise.

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Andrea Rygh Steinsvik



Eirun Hagen Birkeland



Kristine Marie Embretsen

Abstract

The Maritime transportation sector is facing challenges in achieving zero emissions by 2050. Significant reduction in emissions can be accomplished by transitioning from Heavy fuel oil (HFO) to low-carbon fuels such as ammonia, hydrogen and biofuels.

Ammonia has caught the interest as an alternative fuel in the maritime sector due to its characteristics such as zero-carbon emissions. It is also easily stored and filled in tanks, making it compatible with long-distance shipping.

This thesis aims to discuss the different technologies and solutions for blue ammonia production. The objective of this thesis is also to evaluate the performance of ammonia as a maritime fuel from technological, emission and economic perspectives. Main challenges with safety and storage are also considered.

A case study was performed to look at ammonia, HFO and biodiesel on aspects such as emissions throughout their life cycle, effectiveness and costs for utilization. HFO is traditionally the most used fuel in maritime transport and was used as a reference, and biodiesel is a new and upcoming fuel that have a high capacity for emission reduction. The case study involved the chemical/oil tanker Fure Valö which traveled from Mongstad to Reykjavik. This was a middle-length route with the distance of 1,000 NM. The route is already in use by Fure Valö and is a good distance to compare the different fuels to get objective results that were represented in the thesis.

Calculations with the help of MATLAB and tools such as SimaPro were used to present an LCA. The goal of this LCA was to compare the impacts from the life cycle from each fuel. This was used to gain knowledge on which fuel came out as the better alternative to contribute to the process of decarbonization in the maritime sector.

The case study found that to travel the distance from Mongstad to Reykjavik, the volume of ammonia needed was far more than HFO and biodiesel. Between these fuels, ammonia had an overall minimal amount of CO₂ emissions. However, in regards to NO_x, the emissions were quite high compared to HFO and biodiesel. As a result of NO_x tax, CO₂ price and the amount of ammonia required, the cost of ammonia was exceptionally high compared to the traditional and relatively cheap HFO, and to the alternative low-carbon fuel, biodiesel.

Sammenheng

Maritim transportsektor sliter med å oppnå nullutslipp innen 2050. Betydelig reduksjon av utslipp kan oppnås ved å bytte fra Tungolje (HFO) til lavkarbon drivstoff som ammoniakk, hydrogen og biodrivstoff.

Ammoniakk har fanget interessen som et alternativt drivstoff i den maritime sektoren på grunn av dens egenskaper, som nullutslipp av karbon, og hvordan den lett kan lagres og fylles på tanker, noe som gjør den kompatibel med langdistanse shipping.

Målet med denne bacheloren er å diskutere forskjellige teknologier og løsninger for produksjon av blå ammoniakk. Målet er også å vurdere hvordan ammoniakk fungerer som et maritimt drivstoff med hensyn til teknologiske, utslipps- og økonomiske aspekter. utfordringer med sikkerhet og lagring blir også vurdert.

En case-studie ble gjennomført for å se på ammoniakk, HFO og biodiesel når det gjelder utslipp gjennom hele livssyklusen, effektivitet og kostnader for bruk. HFO er tradisjonelt det mest brukte drivstoffet i maritim transport og ble brukt som referanse, og biodiesel er et nytt og fremtredende drivstoff som har et stort potensial for utslippsreduksjon. Case-studien omfattet oljetankeren Fure Valö som reiser fra Mongstad til Reykjavik. Dette er en mellomlang rute med en avstand på 1000 NM. Ruten er allerede i bruk av Fure Valö og er en god avstand for å sammenligne de forskjellige drivstoffene og skaffe objektive resultater som ble representert i bacheloroppgaven.

Beregninger med hjelp av MATLAB og verktøy som SimaPro ble brukt for å presentere en LCA. Målet med denne LCAen var å sammenligne resultatene fra livssyklusen fra hvert drivstoff. Dette ble brukt for å få kunnskap om hvilket drivstoff som var det beste alternativet for å bidra til prosessen med avkarboniseringen i den maritime sektoren.

Resultatet fra casen viser at for å reise fra Mongstad til Reykjavik, trengte man langt mer ammoniakk enn HFO og biodiesel. Av disse drivstoffene hadde ammoniakk generelt en minimal mengde utslipp siden ammoniakk ikke slipper ut CO₂. Imidlertid var utslippene av NO_x ganske høye sammenlignet med HFO og biodiesel. Som et resultat av NO_x-avgift, CO₂-priser og mengde ammoniakk nødvendig, blir prisen på ammoniakk svært høy sammenlignet med den tradisjonelle og relative billige HFO, og til lavkarbon alternativet biofuel.

Nomenclature

Abbreviations

<i>AFC</i>	<i>Alkaline fuel cell</i>
<i>BDC</i>	<i>Bottom dead center</i>
<i>CA</i>	<i>Crank angle</i>
<i>CCS</i>	<i>Carbon capture and storage</i>
<i>CHP</i>	<i>Cogeneration heat and power</i>
<i>CI</i>	<i>Compression ignition</i>
<i>DMFC</i>	<i>Direct methanol fuel cell</i>
<i>EU</i>	<i>The European Union</i>
<i>FC</i>	<i>Fuel cell</i>
<i>GDL</i>	<i>Gas diffusion layers</i>
<i>GHG</i>	<i>Greenhouse gas</i>
<i>HFO</i>	<i>Heavy fuel oil</i>
<i>IC</i>	<i>Internal Combustion</i>
<i>IMO</i>	<i>International Maritime Organization</i>
<i>LCA</i>	<i>Life Cycle Assessment</i>
<i>LNG</i>	<i>Liquefied natural gas</i>
<i>LG-MGO</i>	<i>Low sulfur marine gasoil</i>
<i>MCFC</i>	<i>Molten carbonate fuel cell</i>
<i>MEA</i>	<i>Membrane electrode assembly</i>
<i>MEPC</i>	<i>Maritime Environment Protection Committee</i>

<i>MGO</i>	<i>Maritime gas oil</i>
<i>NG</i>	<i>Natural gas</i>
<i>PAFC</i>	<i>Phosphoric acid fuel cell</i>
<i>PEMFC</i>	<i>Proton Exchange Membrane fuel cell</i>
<i>RPM</i>	<i>Revolutions Per Minute</i>
<i>SCR</i>	<i>Selective Catalytic Reduction</i>
<i>SI</i>	<i>Spark ignition</i>
<i>SOFC</i>	<i>Solid Oxide fuel cell</i>
<i>TDC</i>	<i>Top dead center</i>

Chemical formulas

CH_4	<i>Methane</i>
CH_3CH_2OH	<i>Ethanol</i>
CH_3OH	<i>Methanol</i>
CO	<i>Carbon monoxide</i>
CO_2	<i>Carbon dioxide</i>
CO_3^{-2}	<i>Carbonate ions</i>
H_2	<i>Hydrogen</i>
H_2O	<i>Water</i>
H_3PO_4	<i>Phosphoric acid</i>
N_2	<i>Nitrogen gas</i>
NH_3	<i>Ammonia</i>
NO_x	<i>Nitrogen oxides</i>

N_2O *Nitrous oxides*

O_3 *Ozone*

SO_x *Sulfur oxides*

Glossary of terms

Anthropogenic *Caused by human acitivity*

Terrestrial longwave radiation *Electromagnetic radiation emitted by the Earth's surface and atmosphere*

Symbols

$C_{CO_2 fuel}$ *Cost of CO_2 (USD)*

C_{fuel} *Cost of fuel (USD)*

$C_{NO_x fuel}$ *Cost of NO_x (USD)*

$C_{trans fuel}$ *Cost of transport for fuel (USD)*

d_{ship} *Distance traveled by the ship (m)*

$d_{truck tot}$ *Total distance covered by the trucks used to transport ammonia (km)*

FC_{fuel} *Future cost of fuel with increase in CO_2 price (USD)*

$m_{CO_2 fuel}$ *Amount of CO_2 (kg)*

m_{diesel} *Diesel required to cover the total transportation distance of ammonia (kg)*

\dot{m}_{diesel} *Diesel consumption per km in transportation truck (kg/km)*

$m_{emission}$ *Emissions from combustion (metric tons)*

$\dot{m}_{emission}$ *Emissions of NO_x , SO_x or CO_2 per kg fuel combusted (kg/kg_{fuel})*

m_{fuel} *Fuel required to complete a distance of 1,000 NM (metric tons)*

m_{HFO}	<i>HFO required to complete a distance of 1,000 NM, (metric tons)</i>
$m_{NO_x fuel}$	<i>Amount of NO_x from combustion (kg)</i>
n_{truck}	<i>The number of trucks required to transport ammonia from production site to delivery</i>
P_{CO_2}	<i>Price per kg CO_2 emitted (USD/kg)</i>
P_{diesel}	<i>Price of diesel (USD/L)</i>
P_{fuel}	<i>Price of fuel (USD/kg)</i>
P_{NO_x}	<i>Price per kg NO_x emitted (USD/kg)</i>
SE_{HFO}	<i>Supply energy delivered per kg HFO (MJ/kg)</i>
SE_x	<i>Supply energy delivered per kg biodiesel or ammonia (MJ/kg)</i>
s_{ship}	<i>Average speed provided by the vessel (m/s)</i>
TC_{fuel}	<i>Total cost of fuel (USD)</i>
t_{ship}	<i>Duration to complete the distance by the vessel (h)</i>
V_{fuel}	<i>The volume the fuels will require based on amount (m^3)</i>
V_{truck}	<i>The volume each truck can hold (m^3)</i>
$x\%_{increase}$	<i>Percentage increase in CO_2 price</i>
ρ_{fuel}	<i>The density of the fuels (kg/m^3)</i>

Software

Software	Version	Use
MATLAB	R220B 9.9.0.1538559	Calculations and data visualization
SimaPro	9.3.0.2	LCA and data visualization

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1 Introduction

The earth's atmosphere consists of several greenhouse gases like Carbon dioxide (CO_2), Methane (CH_4), Nitrous oxide (N_2O), water (H_2O) and ozone (O_3).

These greenhouse gases are essential for supporting life on earth. However, due to the increase of human activities such as the burning of fossil fuels and deforestation, starting from the pre-industrial period, have significantly contributed to an increased proportion of terrestrial long-wave radiation (Electromagnetic radiation emitted by the Earth's surface and atmosphere) being trapped by the atmosphere. Consequently, this has resulted in an increase in surface air temperature over the past century [15].

If the increase in these greenhouse gases continues at the current rate, and no sufficient mitigation and adjustments are made, it will lead to significant environmental disruption. Events such as extreme weather and rising sea levels will happen more frequent [4].

To avoid harmful anthropogenic interference (Caused by human activity) in the climate, The European Union (EU) proposed in 1996 that the global mean temperature should not exceed a 2°C increase above pre-industrial temperature levels [119]. The emissions resulting from energy production are critical, and in order to limit the global temperature increase to 2°C means that the industrial nations needs to achieve a 75% reduction in carbon emissions by 2050 [4].

The transportation sector alone contributed to 7 Gt of CO_2 emissions in 2020 and has considerable potential to reduce emissions [98]. Maritime transport is the leading energy-effective transport method and accounts for 80% of global goods transportation [132]. In 2020, maritime shipping was accountable for 830 Mt CO_2 emissions, representing 2.5% of total energy sector emissions. Furthermore, maritime transportation will likely increase with 3.3% annually from 2020 to 2050 [98].

Shipping is, due to the lack of available low-carbon options, and the long lifespan of ships, struggling to achieve zero emissions by 2050. While the long lifespan of ships is generally beneficial for sustainability, in this context, it can also be a negative factor. Older ships with mechanisms and engines that require fossil fuel remains operative. However, significant reduction in emissions can be accomplished by switching to low-carbon fuels like ammonia and hydrogen. Currently, internal combustion engines for ammonia-fueled ships are being developed signaling the beginning of a greener maritime transport sector [98].

1.1 Objective

The main objective of this thesis is to evaluate the viability of blue ammonia production and identify the most optimized method, considering emissions, technological and economic aspects as well as safety considerations. Additionally, the thesis intends to determine whether ammonia is competitive as an alternative green fuel for the maritime sector. This evaluation is conducted through a comprehensive literature review and a case study.

1.2 Case study

In this case study, the aim is to compare the differences in emissions, cost and technological aspects associated with ammonia, HFO and biodiesel used on the ship Fure Valö provided by Furetank. Furetank is a shipping company that emphasizes environmental sustainability and efficiency. The specific voyage considered is from Mongstad in Vestland county, Norway to Reykjavik in Iceland resulting in a total distance of 1,000 nautical miles (NM). Fure Valö is equipped with a Wärtsilä 9L34DF 4,500 kW engine, which is a dual-fuel four-stroke engine.

The case study involved an examination of current and prospective technologies associated with ammonia production, with the objective of choosing the production method that is the most optimal. These findings served as the basis for all major choices made. Safety details and other challenges are discussed. The final outlook of the study aims to be a complete review of ammonia as fuel in the maritime transport sector.

1.3 Structure of the thesis

Chapter 2 introduces the theoretical background needed to understand why one are interested in ammonia. Additionally, will the chapter give a brief overview of the historical development of internal combustion engine and fuel cells and their fundamentals.

Chapter 3 focuses on the different production routes, from energy to storage. It also explores the necessary modifications required for efficient utilization of ammonia in engines. Furthermore, the chapter addresses the safety considerations and challenges associated with using ammonia as a fuel. Lastly, the current and future ammonia production and market are presented.

Chapter 4 will provide a case study for an ammonia-powered vessel traveling a certain distance. The case study will primarily center around the technological aspects, including economic calculations and emissions. Moreover, emissions assessment will be conducted to assess the environmental impact of using ammonia as fuel. Lastly, recommendations for further work are showcased in Chapter 5.

2 Background

There are several other fuels that are currently being used or are on the verge of being utilized, in addition to ammonia. This section provides information on alternative fuels including a brief explanation of their characteristics and production methods. These fuels will further be discussed and compared with each other, aiming to understand the reasons for choosing ammonia as the preferred option. Moreover, this section will provide an overview of the historical development of engines and fuel cells, along with their fundamentals.

2.1 Alternative fuels

The world's oceans are covered by one hundred thousand giant vessels, transporting 60-80% of all international trading [80]. This results in annual emissions of around 940 million metric tons of CO₂. The maritime sector is accountable for 2.5% of global greenhouse gas (GHG) emissions [115]. The most commonly used fuel is heavy fuel oil (HFO), which leads to high GHG emissions. The emissions are expected to increase with 130% within 2050 if the decarbonization process is not urgently implemented [145]. The primary motivation for exploring alternative fuels is the requirements from International Maritime organization (IMO) and Maritime Environment Protection Committee (MEPC), which mandate a 50% reduction in maritime emissions by 2050 [75]. This necessitates considering alternative fuels to reduce ship emissions. All alternatives comes with benefits and drawbacks regarding safety, emissions, feasibility and cost [80].

Table 2.1 provides an overview of some of the key components of the fuels and serves as a foundation for comparison. It is crucial to note that there is a significant variation in emission per km of combustion. The following sections will explain the fuels briefly.

Table 2.1: Comparison of components related to the different fuels [79, 47, 29].

Fuel	Supply energy (MJ/kg, LHV)	Energy density (MJ/L, LHV)	Relative tank volume	CO ₂ emission from complete combustion (g CO ₂ /km)	SO _x emission from complete combustion (g SO _x /km)
HFO	40.5	35	1.00	49	0.36
MGO	42.7	36.6	-	42	-
LNG	50	22	1.59	37	0.02
Hydrogen	120	8.5	2.76	0	0
Battery	0.29	0.33	106.1	0	0
Methanol	19.9	15	2.33	43	0.02
Ethanol	26	21	1.75	-	-
Biodiesel	37.8	34	-	-	-
Ammonia	18.6	12.7	2.76	0	0

2.1.1 HFO

HFO, which is obtained through distillation of crude oil, is primarily used as marine fuel [88]. It serves as the main source of power for ship engines, and has been widely utilized in the maritime sector since the 1960s [41]. It was reported in 2020 that approximately 60% of the around 60,000 large ships relied on HFO as fuel for transport across the world's oceans. The primary reason for this is its relatively lower cost, it is around 30% cheaper than alternative fuels [41]. The shipping industry has grown accustomed to the wide availability and affordability of HFO. However, it is important to mention the hazards associated with HFO, and why it is important to start investing in cleaner alternative fuels. HFO is highly polluting, and poses significant risks to both humans and wild life due to its highly toxic nature [41]. There is a high concentration of sulfur in HFO, making the shipping industry account for 8% of global sulfur dioxide (CSO_2) emissions. It becomes highly acidic when combined with water. This leads to the shipping industry being a large contributor to acid rain and respiratory diseases [41].

2.1.2 MGO

Maritime gas oil fuel (MGO) has been regarded as the "clean fuel" within the maritime industry [10]. MGO distinguishes itself from HFO by not requiring heating during storage. Marine fuels exclusively consist of distillates. Distillates can be explained as all the components of crude oil that evaporate in distillation to further be condensed from gas to liquid [104]. The sulfur content in MGO can vary, with a maximum permissible value of 1.5% which is lower than that of HFO. As efforts are made to reduce sulfur emissions in the marine sector, options like low sulfur marine gas oil (LG-MGO) become more attractive as a fuel choice. The sulfur content LG-MGO is less than 0.1% [104].

There are certain drawbacks associated with MGO. Firstly, the presence of water in the fuel can lead to the growth of fungi and bacteria. This can result in clogged filters and erratic engine operation. Secondly, the viscosity of MGO is considerably lower compared to the design of the fuel pumps in marine engines. Such a significant difference in fuel viscosity can lead to an increase in fuel leakage between the pump plunger and barrel [10]. Despite having lower CO_2 -emissions than HFO, as shown in Table 2.1, the emissions are still relatively high when compared to other alternative fuels.

2.1.3 LNG

Liquefied natural gas (LNG) has been portrayed as a green and clean fuel, although this has been criticized as a form of green-washing by the fossil gas industry. The greenhouse gas emissions are reduced to an extent by using LNG instead of HFO, and it has for that reason, long been considered the cleanest fuel in the maritime sector. LNG is suitable for all vessel types in the

maritime sector. It is considered to be a safe and proven technology with low operational and maintenance costs and high energy content [68].

LNG is essentially natural gas (NG) that has been cooled down to -161°C . The advantage of converting NG into liquid form is that it reduces its volume to approximately 1/600th of NG. This makes LNG severely attractive for transportation purposes [135]. NG is being considered as a potential fuel for the future due to its lower emissions compared to coal, which is the most polluting fossil fuel. However, it is important to note that NG still contributes to high GHG emissions. Throughout the various stages of the NG supply chain, methane, a potent greenhouse gas, is often leaked into the atmosphere. Methane emissions alone have accounted for more than a quarter of global warming to date [153].

2.1.4 Hydrogen

Hydrogen is being viewed as a fuel for the future, because it is considered to be clean, flexible and energy-efficient [46]. When hydrogen is used as fuel, no CO_2 is emitted. Hydrogen-powered fuel cells play a crucial role in this context, as they utilize hydrogen (H_2) and oxygen (O_2) to convert the chemical energy stored in the fuel cell into energy, water, and heat [125]. This process is carbon-free, and only releases water vapor as a byproduct. Fuel cells operate similarly to batteries, the difference is that as long as fuel is supplied the fuel cells will produce electricity and heat [123].

Hydrogen can be produced from various sources using different processes, which are discussed in more detail in Section 3.1.1. The production of hydrogen itself is associated with varying degrees of CO_2 -emissions, depending on if it is categorized as gray, blue or green hydrogen. Currently, 96% of hydrogen production falls under the gray category. Studies indicate that producing 1 kg hydrogen using fossil-based energy leads to the generation of 9.3 kg of CO_2 during the process [120]. However, if Carbon Capture and Storage (CCS) technology is employed during the production process, it has the potential to reduce CO_2 emissions by nearly 90%. For hydrogen to be a clean fuel, the production state need to cut the emissions [113]. This means that it needs to be a higher focus on producing at least blue, but ideally green hydrogen forward. Green hydrogen are produced with renewable sources and electrolysis, but its current cost-effectiveness is limited.

For hydrogen to be liquefied it requires a temperature as low as -253°C [100]. Keeping hydrogen in its liquid form necessitates significant energy expenditure. This disadvantage is primarily related to transport of hydrogen, and refilling when used as fuel. This is why most hydrogen today is produced in the same place it is used [113].

2.1.5 Electrical power

Electrified shipping is coming more into light in the maritime market, as the fossil-fueled ships are being phased out to a larger degree [122]. This development brings several advantages. Firstly, it can lead to reduced emissions and fuel consumption, contributing to a cleaner and more sustainable maritime industry. Additionally, electrification allows for more flexible ship designs, and less maintenance required for the machinery [94]. Another advantage of using electricity is the elimination of the risk of fuel spills. Electrically powered ships travel quietly and there won't be any smell from fumes [60]. These benefits make electrification an attractive option for the future of shipping.

Electrifying the maritime sector does come with certain drawbacks. One of the challenges is the time and capacity required for recharging. Batteries used on vessels that travel long distances would need to store large amounts of energy. These would take up a significant amount of space on the vessel. To address this issue, a solution being explored is combining fuel cells with batteries [130]. Fuel cells function similarly to batteries, but the key difference however, is that they do not run out and therefore do not require recharging [54]. This is explained more in depth in Section 3.6.1. When considering batteries as the primary option for electrification, there are several limitations. The infrastructure would need significant changes, extending beyond simply changing the fuel type. This would among other things require charging stations, making the initial investment cost high. Another disadvantage is that this will be more time consuming, it takes longer to recharge than to refuel today [65].

2.1.6 Biofuel

Biofuels has gotten more attention as alternative fuels sources, in several transportation sectors, including the maritime sector. Biofuel are derived from biomass, which can include plant or algae material as well as animal waste. These feedstocks is considered renewable because of its ability to replenish rapidly, leading to biofuel being referred to as a renewable fuel [129].

Biofuel can be categorized into various types, with biodiesel and ethanol being the two most common forms. Biodiesel exhibits similar performance characteristics to petroleum diesel fuel. The process and alteration of biomass makes biodiesel a liquid fuel. This makes it easy to replace petroleum diesel which will significantly reduce carbon emissions through its lifecycle [118]. Biodiesel offers flexibility in its usage and can be blended with petroleum diesel at different concentrations. For instance, pure biodiesel is referred to as B100, indicating it contains 100% biodiesel. B20, another blend, has the ratio of 20% biodiesel and 80% petroleum diesel and is a commonly used blend.

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is another widely used biofuel. It is mostly used in a blend of ethanol and

gasoline which reduce the air pollution. Ethanol is a clear and colorless liquid, and its chemical structure does not change regardless of what feedstock from which it is produced. The use of ethanol helps reduce air pollution as it is derived from renewable sources. However, it should be noted that ethanol has a lower energy content compared to gasoline [52].

Biofuel offer several benefits, with it being a feasible and flexible alternative to phasing out petroleum diesel. However, there are major concerns associated with biofuel, including cost, supply guarantee, and sustainability. One of the challenges with biofuels is that they are still in the early stages of development, and their performance characteristics are not yet fully understood. Extensive testing and research are required to ensure their optimal performance and compatibility with existing infrastructure. Another concern is the potential competition for resources with other sectors such as food production. The development of biofuels may be limited by high water demand and land use [32]. The benefits and drawbacks will be considered more in depth through a case study in Section 4.

2.1.7 Methanol

Methanol (CH_3OH) is currently gaining attention as a potential alternative fuel for the future in the transportation sector. Methanol has similar chemical and physical fuel properties as ethanol. Methanol was in use as commercial transportation fuel in the 1990s but its development stagnated. However, it is now being reconsidered as a viable alternative. There are several benefits associated with using methanol as a fuel. One advantage is its lower production cost compared to other fuels. Additionally, methanol has a lower risk of flammability compared to gasoline, which enhances safety considerations. Lastly it has an increased energy security since it can be manufactured from several different carbon-based feed stocks including biomass, natural gas and coal [51]. Methanol is a non-cryogenic liquid at ambient temperatures, making it relatively easy and cheap to handle. It does not require refrigeration or specific and expensive materials for tanks and pipes. The expertise and technology exists already, so bunkering would be easy to implement [117].

One of the downsides with methanol, compared to HFO and LNG, is that it require more space onboard. Up to two-and-a-half times more space is needed to store methanol. Although the space requirements may be a challenge, the main challenge with methanol as fuel lies in how to produce green methanol, and availability when needed [137].

2.2 Historical development of combustion engines and fuel cells

This section provides a brief overview of the historical development of combustion engines and fuel cells.

Combustion engines

In 1508, the famous Leonardo da Vinci sketched the "fire engine". The idea was to explore a method of lifting heavy weight using fire. The sketch consisted of a solid cylindrical vessel and was installed with a piston fitted with leather seals. The idea was that gunpowder would be inserted into the cylinder while the piston was situated at top-center crank position (TC). The charge would be ignited through a narrow hole and the gunpowder would then explode which causes the piston to move downwards. The expansion would decrease the temperature and the pressure of the gases in the cylinder. Then the atmospheric pressure would press the piston up, lifting the weight [72]. Leonardo da Vinci is credited with inventing the atmospheric reciprocating internal combustion engine, although he did not build the actual engine [72].

The Dutch physicist Christian Huygens was the first to build a gunpowder engine in 1673. The engine consisted of a tin-plated metal sheet which where lined with a layer of plaster. The piston was also sealed with leather similar to the invention by da Vinci. The leather was wetted and put on top of the cylinder and functioned as valves [72].

Christians Huygens assistant, Denis Papin, continued with the engine and improved the original design. One of his notable contributions was the addition of an exhaust valve in the piston. He was also the one who found out that with this particular design, about 20% of the charge was left in the cylinder as residuals [72].

Robert Street developed the first recorded engine in 1794, which used combustion of a vaporized fuel-air mixture within a cylinder to produce continuous reciprocating piston movement. This movement did not rely on atmospheric pressure. The engine had a cast-iron-open-top cylinder that was heated underneath by a solid-fuel stove, and a cast-iron piston that worked a water pump [72].

The first internal combustion engine (IC-engine) for commercial use was developed by the Belgian-French engineer Jean J. Lenior in year 1858. This engine was a two-stroke engine where a coal gas and air mixture were drawn into the engine cylinder during the first half of the piston stroke. From that, the charge was ignited by a spark [61].

In 1862, Frenchman Alphonse Beau de Rochas described the fundamentals of four-stroke cycle and the maximum efficiency that could be achieved in IC engines. Inspired by Beau de Rochas, Nikolaus August Otto successfully implemented the four-stroke process in 1876 [16, 28]. This engine had a significant advantage over the gasoline engine built by Étienne Lenoir because it

utilized precompression of the mixture [16].

In 1892, the German engineer Rudolf Diesel developed an engine in which a high compression ratio was utilized to ignite the fuel. The efficiency of the engine was increased as a result of higher compression and expansion ratios. Today's diesel engine is based on the same principle, and two-stroke and four-stroke diesel engines have been developed [69].

Figure 2.1 illustrates a timeline of the historical development of combustion engines.

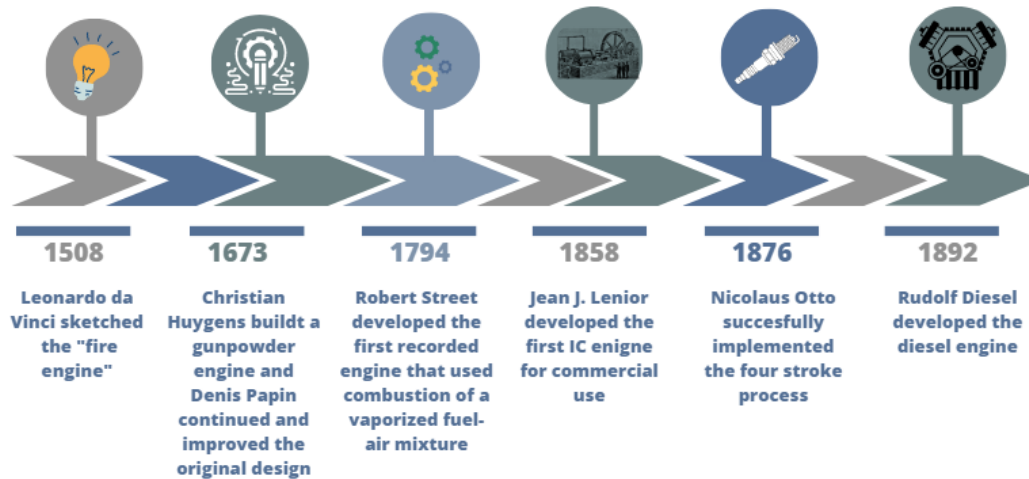


Figure 2.1: Timeline of the history of combustion engines.

Fuel cells

The development of fuel cells dates back over 180 years to 1839 when Sir William Robert Grove demonstrated the principle of fuel cells [110]. The interest in fuel cell research persisted, but at that time, practical fuel options were limited to coal. As a result, efforts were primarily focused on developing a fuel cell that could utilize coal, although this task was eventually deemed unachievable. In 1889, Ludwig Mond and Carl Langer made significant improvements to Grove's cell and built the first modern fuel cell. They were also the first to use the name "fuel cell" [83].

In 1933, the English engineer Sir Francis Thomas Bacon began his work on fuel cells [110]. The first fuel cell he developed utilized hydrogen and oxygen. This fuel cell operated by converting air and hydrogen directly into electricity through electrochemical processes [9].

The Proton Exchange Membrane fuel cell (PEMFC) was invented by Dr. William T. Grubb in 1955 while he was working on modifications to the initial design of the fuel cell. Alongside Dr. Leonard Niedrach, they successfully developed the first fuel cell that could effectively operate with a wide range of affordable hydrocarbon fuels [110].

In 1958, Bacon presented an alkaline fuel cell to the Britain's National Research Development Corporation. Despite its high cost, the fuel cell demonstrated sufficient reliability to impress

Pratt & Whitney, a renowned company specializing in propulsion systems and advanced aircraft [152]. As a result, Pratt & Whitney acquired the patent for Bacon's fuel cell technology, which was subsequently used in the Apollo spacecraft [9].

Bacon's work laid the foundation for extensive research and development in the field of fuel cells. In the 1980s, there was a renewed interest in fuel cells, driven largely by growing environmental concerns associated with the combustion of fossil fuels. Since then, fuel cell technology has been extensively studied and researched worldwide. Today, fuel cells are already being utilized in various applications, including vehicles, boats, and power generation for critical facilities such as hospitals and banks [83].

Figure 2.2 illustrates the historical development of fuel cells.

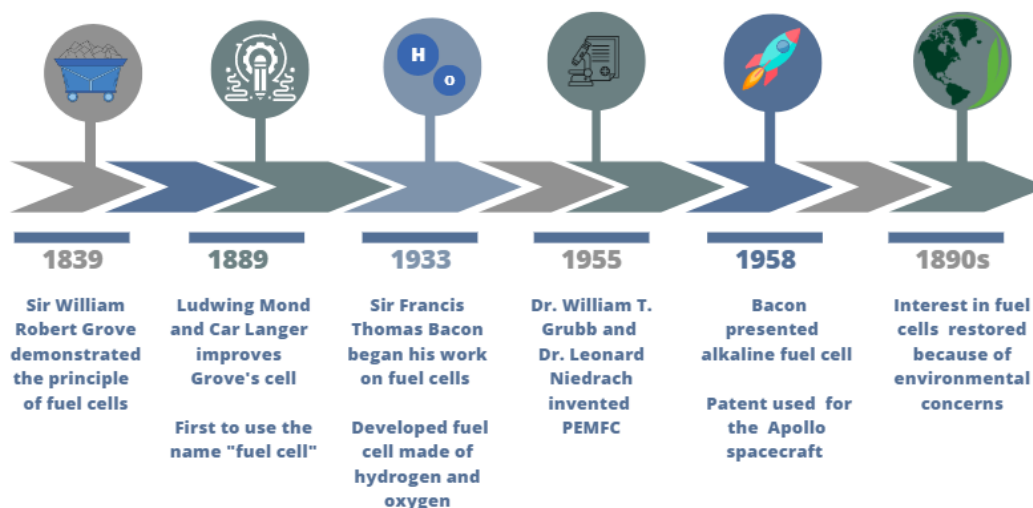


Figure 2.2: Timeline of the history of fuel cells.

2.3 Today's internal combustion engine (IC-engine)

IC-engines are defined as engines in which the chemical energy of the fuel is released inside the engine and directly utilized for mechanical work [61]. IC-engines are widely used, particularly in motor vehicles and maritime transportation, but they are applied in various other fields as well, as shown in Appendix A.1. These engines are typically reciprocating engines, meaning that they operate with a piston moving back and forth within a cylinder, transmitting power to a drive shaft through a connecting rod and crankshaft mechanism. The valves are used to control the intake and exhaust of gases within the engine [61].

Compression ignition and spark ignition engines

There are two main types of IC-engines: compression ignition (CI) engines, commonly known as diesel engines, and spark ignition (SI) engines, commonly known as Otto, gasoline, or petrol engines [108]. In traditional SI engines, the air-fuel mixture is induced into the cylinder and

compressed near top dead center (TDC). Combustion is initiated by an electric discharge at the spark plug, and flame propagation occurs in a premixed air-fuel mixture [13]. In contrast, CI engines have fuel directly injected into the cylinder, which automatically ignites due to the high ambient temperature at the end of the compression stroke. In larger vessels, CI engines are predominantly used, regardless of whether they are four-stroke or two-stroke engines [69].

2.3.1 Two and four-stroke engines

Both two and four-stroke engines are widely used in both the small-sized engine market and the very large engine market. An overview of the applications of these engines can be found in Appendix A.1. In this section, the fundamentals of the two and four-stroke engine are presented.

Two-stroke engine

In Figure 2.3(A), the area above the piston near TDC shows the captured air and fuel charge. The spark plug ignites this mixture, resulting in a rapid increase in pressure and temperature that drives the piston downward illustrated in Figure 2.3(B). Meanwhile, the open inlet port beneath the piston allows air from the atmosphere to be drawn into the crankcase as the crankcase volume expands, reducing the pressure [21].

In Figure 2.3(C), as the piston approaches Bottom Dead Center (BDC) and the exhaust port opens, a high-pressure exhaust gas pulse is released into the exhaust duct as a result of the combustion process. Simultaneously, the fresh charge below the piston undergoes compression, which is known as the scavenge process [21]. During this process, a certain amount of fresh charge escapes without being burnt [21]. The escaping of the fresh charge occurs as the piston moves upward, creating a pressure difference that allows the fresh charge to enter the cylinder and displace the remaining exhaust gases [25, 69]. When the exhaust port is closed, the compression begins until the combustion process is started by ignition [21].

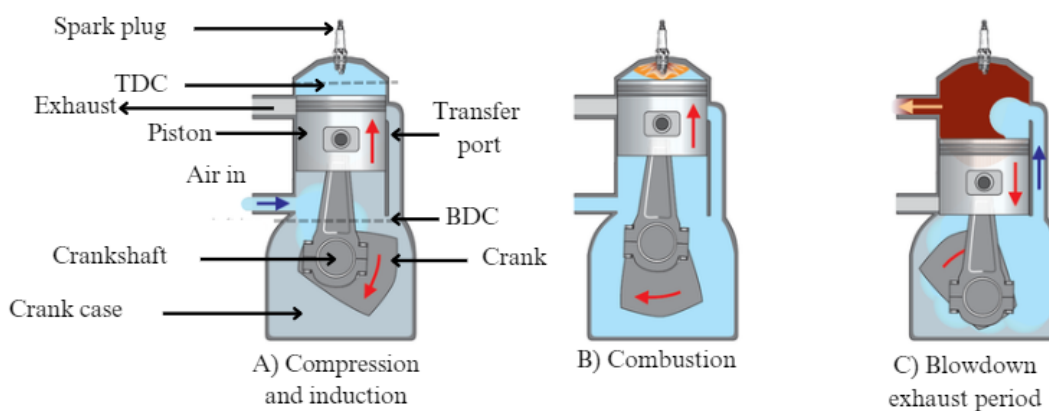


Figure 2.3: Two-stroke engine process with A) compression and induction, B) Combustion and C) Blowdown exhaust period [127].

Four-stroke engines

The four-stroke process, unlike the two-stroke process, requires two additional strokes to remove the combustion gases from the working chamber [16]. As a result, a total of 720°CA (Crank angle) is needed to complete one cycle [69].

Figure 2.4(A) shows the intake valve on the left, which is controlled by the movement of the rotating camshafts that push the tappet and valve spring. The intake valve opens at TDC, reaches its maximum lift at mid-stroke, and closes at BDC. As the piston moves from TDC to BDC during the intake stroke, the cylinder is filled with air from the atmosphere. This air becomes trapped within the cylinder, and as the piston moves from BDC to TDC during the compression stroke (shown in Figure 2.4(B)), the volume decreases to its minimum. Consequently, the pressure and temperature of the air rise, and the fuel trapped with the air vaporizes [20].

At the end of the compression stroke, combustion takes place, initiated by a spark from the spark plug. As a result, the pressure within the cylinder rises rapidly, leading to an increase in temperature. Due to the high pressure difference between the upper side, the piston moves downwards, generating a torque on the crankshaft. Figure 2.4(C) illustrates this process [20].

Now, the cylinder contains the products of combustion, and these gases need to be expelled. This is achieved by lifting the exhaust valve, allowing the upward sweeping movement of the piston to push out the exhaust gas. This process occurs during the exhaust stroke as the piston moves from BDC to TDC, resulting in a decrease in cylinder volume. Figure 2.4(D) illustrates this stage [20]. It is worth noting that the four-stroke engine offers greater maneuverability compared to a two-stroke engine [8].

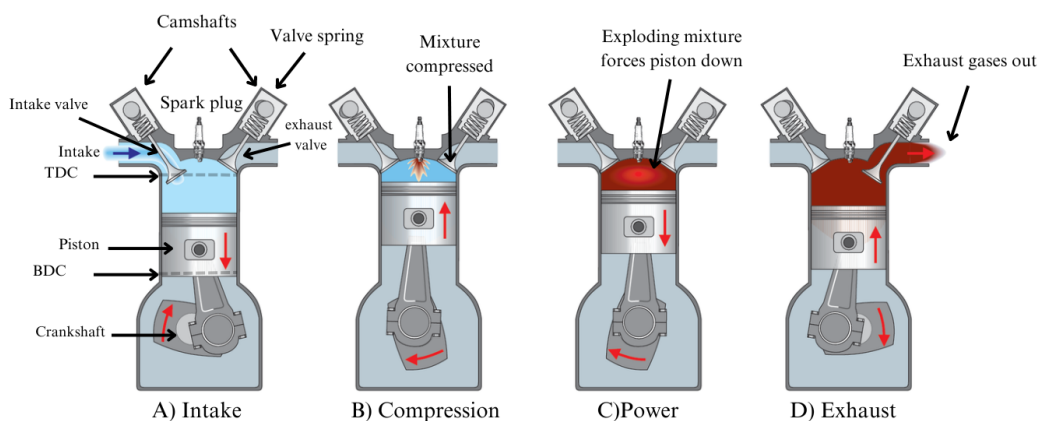


Figure 2.4: Four-stroke engine process with A) Intake, B) Compression, C) Power and D) Exhaust [127].

In Table 2.2 the four-stroke and two-stroke engine is compared to each other in the categories power, size, weight, cost, efficiency, maintenance and usage.

Table 2.2: Comparison between four and two-stroke engines in regards to power, size, weight and cost, efficiency, maintenance and usage [69, 8].

	FOUR-STROKE	TWO-STROKE
Power	<ul style="list-style-type: none"> • One power stroke in every two revolutions of the crankshaft as the cycle is completed in four-strokes or in two revolutions of the crankshaft • For the same size engine, power produced is less and for the same power output, the engine is bigger in size. 	<ul style="list-style-type: none"> • One power stroke in each revolution of the crankshaft as the cycle is completed in two strokes or in one revolution of the crankshaft. • For the same size engine, power produced is more and for the same power output, the engine is smaller in size. • No valve mechanism and light in weight makes the initial cost low.
Size, weight and cost	<ul style="list-style-type: none"> • Heavy weight and complicated valve mechanism makes the initial cost is high. • One power stroke in two revolutions of the crankshaft makes the turning movement of the shaft non-uniform and as a result it needs a heavier flywheel to rotate the shaft uniformly 	<ul style="list-style-type: none"> • Less moving parts in the engine results in less rotating mass, therefore a higher potential acceleration given the same horsepower used by a four-stroke. • The turning movement of the shaft is more uniform and as a result, it needs a lighter flywheel to rotate the shaft uniformly.
Efficiency	<ul style="list-style-type: none"> • Thermal efficiency and volumetric efficiency is higher • Used where high efficiency is important • Usually water-cooled, therefore the deterioration is less. 	<ul style="list-style-type: none"> • Has lower thermal efficiency and volumetric efficiency.
Maintenance	<ul style="list-style-type: none"> • Uses less lubricant. • Lubricant is in the crankcase, therefore not mixed with the fuel 	<ul style="list-style-type: none"> • Usually air-cooled, therefore deterioration is more. • Needs more lubricant.
Usage	<ul style="list-style-type: none"> • Used where high efficiency is important as in vehicles, power generation and aeroplanes. • Became a popular choice in marine vessels, but was overtaken by the two-stroke engine. • Consumes fuel per four strokes 	<ul style="list-style-type: none"> • Used in large vessels because of low weight and compactness • Profitable option for merchant and cargo ships. • Consumes fuel per two strokes and also had the advantage of being able to burn low-grade fuel oil

2.3.2 Potential improvements for IC-engines

IMO is the globally recognized authority for setting standards and regulations regarding the safety, security, and environmental performance of international shipping [105]. In recent years, there has been a search for alternatives to meet the IMO requirements by improving the fuels and engines commonly used. One technology that has emerged is scrubbers, which are capable of removing SO_x emissions through an exhaust gas cleaning system. The engine exhaust gas is directed through chambers containing a "scrubbing cloud" of water, where water droplets react with SO_2 , effectively removing it. This implementation can eliminate over 80% of particulate matter that would have otherwise been emitted. However, scrubbers have some drawbacks. They can be expensive to install on ships, and if the water used for the scrubbing process is not properly discharged and treated, it can contribute to water pollution [159, 97].

Another regulation enforced by IMO pertains to controlling NO_x emissions from marine engines [105]. To address this, Selective Catalytic Reduction (SCR) technology can be employed to cleanse the exhaust. SCR utilizes catalyst elements and a reducing agent to significantly reduce NO_x emissions. With this technology, it is possible to achieve up to a 95% reduction in NO_x during the combustion process [158, 148].

For ships fueled by HFO, CCS can be seen as a potential game changer. While it is possible to remove SO_x and NO_x through other technologies, complete elimination of CO_2 emissions during combustion is not achievable. However, this challenge can be addressed by capturing CO_2 before it is released into the atmosphere. The concept involves capturing CO_2 from the main engine before it passes through the exhaust outlet. This technology has the potential to significantly enhance the sustainability of HFO as a fuel, making it a more environmentally friendly option than it currently is [22].

CCS is also feasible with MCFCs. These fuel cells have the capability to utilize exhaust gases from power plants on the cathode side. In the presence of flue gases abundant in CO_2 , the cathode can consume CO_2 while it is produced at the anode through fuel cell reactions. The anode outlet stream consists mostly of CO_2 and water, enabling the potential for high-purity carbon capture and recovery. Notably, the MCFC is the only post-combustion CCS system with energy production, unlike other conventional CCS systems that require power input. The distinctive aspect of this particular fuel cell has attracted significant attention from researchers in recent years [93].

2.4 Fuel cells in maritime transport

Fuel cells are regarded as environmentally friendly technology that can address the current environmental concerns, such as high levels of pollutants. Due to their potential to minimize environmental impact, fuel cells have emerged as a viable alternative to combustion engines [161]. Fuel cells convert chemical energy directly into electrical energy and heat, bypassing the indirect pathway through thermal energy used by combustion engines. Moreover, fuel cells operate with simplicity and higher efficiency compared to IC-engines [161, 18].

Fuel cell technology is based upon the basic chemical reaction shown in Equation 2.1 below.



The basic design of a fuel cell includes an anode for fuel supply, a cathode for oxidant supply, and an electrolyte that facilitates the movement of ions between the anode and cathode [161].

2.4.1 Fuel cell types

The categorization of fuel cells is determined by the type of electrolyte utilized. The electrolyte plays a crucial role in determining the operating temperature and power output of the fuel cell. Each type of fuel cell has its own advantages and limitations, which determine their suitability for various applications [18, 91]. Energy generators employing fuel cells must adhere to the specified energy requirements, taking into account factors such as vessel size and distance traveled [91].

A variety of different fuel cell types with unique characteristics have been developed, offering diverse options for various applications. Based on the choice of electrolyte and fuel, there are six different types of fuel cells currently available [89].

- Proton Exchange Membrane (PEMFC)
- Solid oxide fuel cell (SOFC)
- Phosphoric acid fuel cells (PAFC)
- Molten carbonate fuel cell (MCFC)
- Alkaline fuel cell (AFC)
- Direct methanol fuel cell (DMFC)

Among the various fuel cells available in the market, the following types have gained commercialization and are commonly used in marine applications today, and are considered to be promising in this sector [155, 156].

Proton Exchange Membrane fuel cell (PEMFC)

PEMFC are fueled with pure hydrogen and utilize a Proton Exchange Membrane (PEM). Positioned at the core of the fuel cell is the membrane electrode assembly (MEA), which comprises a polymeric material. The MEA incorporates catalyst layers and gas diffusion layers (GDL). The GDL facilitates the diffusion of reactants to the catalyst and serves as the electrical conductor for electron transportation to and from the catalyst layer [87].

PEMFCs are known for their high electricity production efficiency, which can reach up to 65% with minimal heat generation. One notable advantage of PEM cells is their quick response and short start-up time. These characteristics stem from the low-temperature reaction that takes place within the cell, typically ranging from 60°C to 100°C [18]. PEMFC is already widely used in electric vehicles and offers advantages such as compactness, lightweight design, and decreasing costs [107].

Solid Oxide Fuel Cell (SOFC)

SOFCs have a membrane composed of an oxide ceramic. The solid electrolyte is positioned between two porous electrodes, the anode and cathode. The basic operation of SOFCs relies on the oxidation of fuel and the reduction of oxygen, which take place at the anode and cathode electrodes, respectively [89]. The anode side supplies the fuel, while the oxygen is sourced from the cathode side, as illustrated in Figure 2.5.

The SOFC operates at high temperatures, typically ranging from 500°C to 1000°C. This type of fuel cell exhibits a high efficiency, varying between 40% and 60% [144]. However, a drawback is the extended start-up and shut-down time of the cell. As a result, SOFCs are primarily employed for auxiliary power units and medium to large-scale power generation applications [144]. Additionally, SOFCs demonstrate a strong tolerance towards fuel contaminants such as carbon monoxide and sulfur compounds, enabling them to utilize various fuel types [18].

Phosphoric acid fuel cell (PAFC)

PAFC is the most commonly used and extensively researched type of fuel cell, often referred to as the "first generation" of modern FCs. In a PAFC, hydrogen is supplied to the anode of the fuel cell. The electrolyte primarily consists of phosphoric acid (H_3PO_4), which serves as a proton conductor. This allows the protons to move from the anode to the cathode, while the electrons flow through an external circuit. At the cathode, air is supplied, where oxygen reacts with the protons and electrons originating from the electrolyte and the external load. Platinum is required as an electro-catalyst in both the anode and cathode for this configuration [101, 56, 144].

The operating temperature of PAFCs typically range between 150 and 200°C. In comparison to PEMFCs, PAFCs demonstrate greater tolerance for impurities and exhibit higher overall efficiency. When used for co-generation of electricity and heat, PAFCs can achieve an efficiency of over 85%. However, when generating electricity alone, the efficiency drops to approximately 40% [101, 56]. The primary drawback of PAFCs is their lower power output compared to other fuel cell types of the same weight and volume. As a result, PAFCs are typically larger and heavier. Additionally, these fuel cells can be costly to manufacture and operate. They require a larger quantity of expensive platinum catalyst compared to other fuel cell types, which significantly increases the overall cost.[56].

Molten carbonate fuel cells (MCFC)

MCFCs are high-temperature fuel cells that operate in the range of 650-700°C. These fuel cells utilize a molten electrolyte composed of a mixture of carbonates from alkaline metals. Unlike PAFCs and PEMFCs, MCFCs do not require an external reformer to convert fuels like natural gas and biogas into hydrogen. The transport of ions in MCFCs is facilitated by carbonate ions (CO_3^{-2}) absorbed in the anode and regenerated in the cathode. While PAFCs require expensive platinum as a catalyst, MCFCs utilize nickel and nickel oxide for the anode and cathode, making them a more cost-effective alternative [18, 56, 144].

The primary disadvantage of current MCFC technology is durability. The high operating temperatures and corrosive electrolyte used in these cells accelerate component breakdown and corrosion, leading to a decrease in the cell life span [56]. While the focus of development has mainly been on large stationary applications. The main concern of current MCFC technology is its durability. Despite it using more cost-effective catalysts, it will still face the withdraw of high costs [144, 18].

In Figure 2.5, a schematic representation of a fuel cell is illustrated. Along with the figure, Table 2.3 is provided to further showcase the working principle of the different fuel cells.

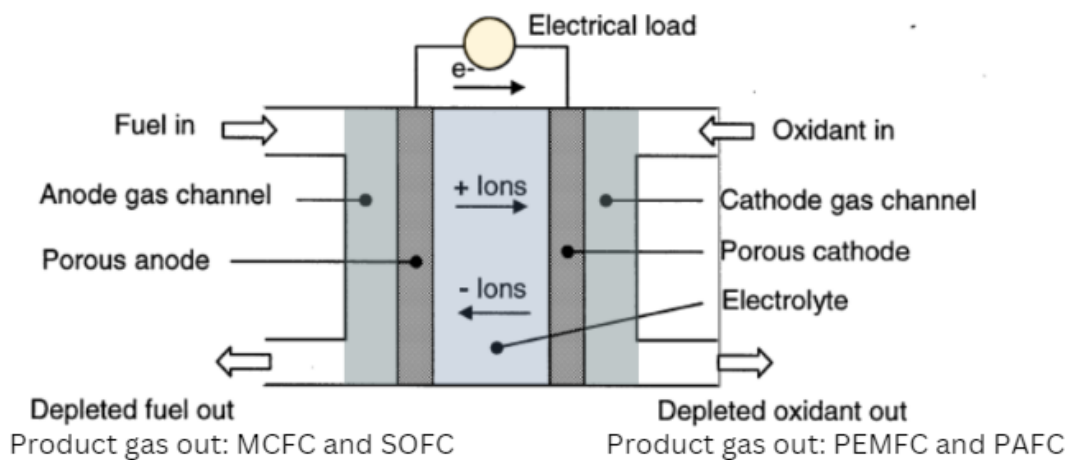


Figure 2.5: Schematic representation of a fuel cell [50].

Table 2.3: Fuel cell characteristics for Figure 2.5 to show the working principle of each fuel cell [50].

Fuel cell type	Anode reaction	Mobile ion	Cathode reaction	Operating temperature °C	Efficiency range %
PEMFC	$H_2 \rightarrow 2H^+ + 2e^-$	H^+	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	60-100	40-70
SOFC	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	O^{2-}	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$	500-1000	40-60
PAFC	$H_2 \rightarrow 2H^+ + 2e^-$	H^+	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	150-200	40
MCFC	$H_2O + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	CO_3^{2-}	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	650-700	30-50

3 Ammonia as a fuel

Ammonia NH_3 is one of the world's most produced chemical compound and it is primarily utilized as a mineral fertilizer in the form of ammonium salts and nitrates [109]. It exists as an colorless gas under ambient conditions, and it has a lower density than air. Its boiling point is at -33.3°C and it can be handled as a liquid by applying moderate pressure [25].

Liquid ammonia is being increasingly used as an energy carrier, and the production of ammonia in maritime transport has garnered greater attention in recent years due to its use as a carbon-free fuel [109]. Ammonia possesses a higher energy density compared to other substances such as liquid hydrogen, and it can be efficiently liquefied through condensation, and stored in tanks [74]. When it comes to shipping, especially over long distances, it is crucial to have a fuel that can be stored with high energy density. This renders battery operation and pressurized hydrogen impracticable for such purposes [74].

Ammonia production can be separated into three types based on the feedstock employed as illustrated in Figure 3.1. Gray ammonia is produced from natural gas or other fossil fuels without carbon capture and storage (CCS). Blue ammonia is produced using natural gas or other fossil fuels, but with CCS implemented. Green ammonia production, on the other hand, is free from CO_2 emission, and electricity from renewable energy sources are used in the electrolysis of water to produce hydrogen for ammonia production [81].



Green ammonia
CO₂ emission-free
Renewable electricity



Blue ammonia
Carbon capture and
storage (CCS)
Fossil sources



Gray ammonia
Natural gas or
other Fossil sources

Figure 3.1: Color terms of ammonia [25].

3.1 Production of Ammonia

The production process of ammonia relies on hydrogen and nitrogen production. There are multiple ways to produce hydrogen, and the most common approach are natural gas reforming and electrolysis. Nitrogen is obtained through air separation, which can be achieved using three different methods. The ammonia itself is produced through a reaction with hydrogen, a process known as the Haber-Bosch method. Figure 3.2 illustrates the different feedstocks and methods involved in the production of hydrogen and nitrogen, which are then utilized in the Haber-Bosch process to produce ammonia [25].

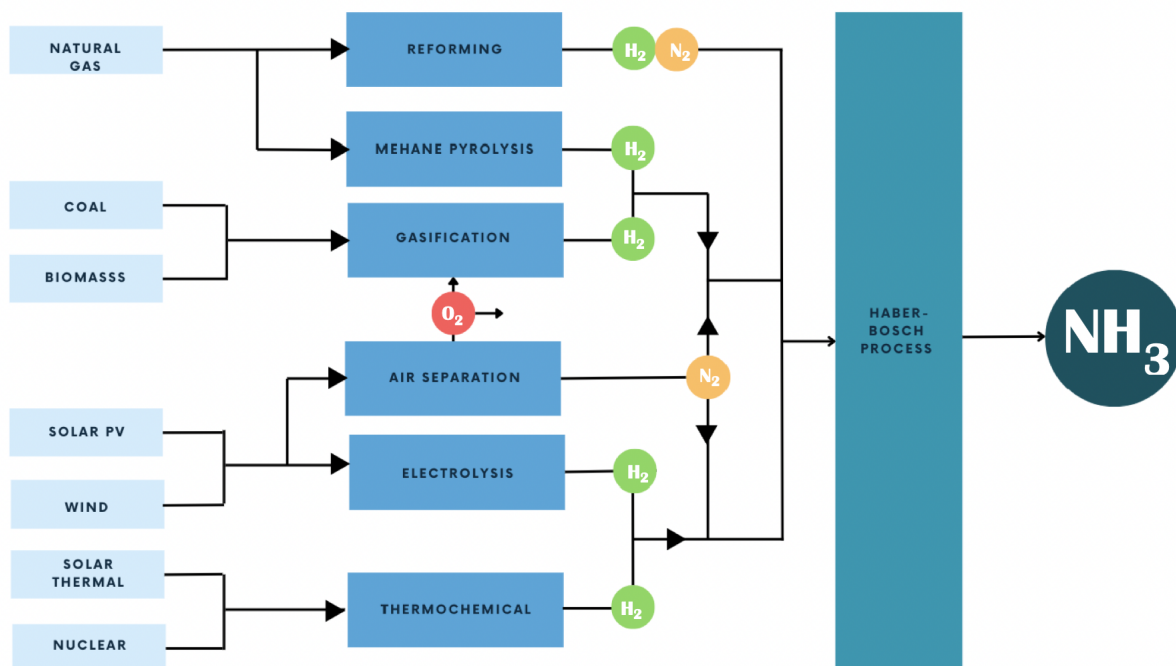


Figure 3.2: Ammonia production process with feedstocks [25].

The reverse process of the Haber-Bosch is known as cracking. This technique is commonly used when hydrogen is stored as ammonia and needs to be separated for utilization. Storage and safety concerns are important aspects to consider when handling ammonia. Figure 3.3 illustrates the estimated ranges of GHG emissions associated with ammonia production from various feedstocks. The current ammonia production methods are mostly fossil based, and ammonia are primarily used as fertilizer. However, future ammonia production has the potential to reduce GHG emissions and find new applications as a fuel and hydrogen carrier [79].

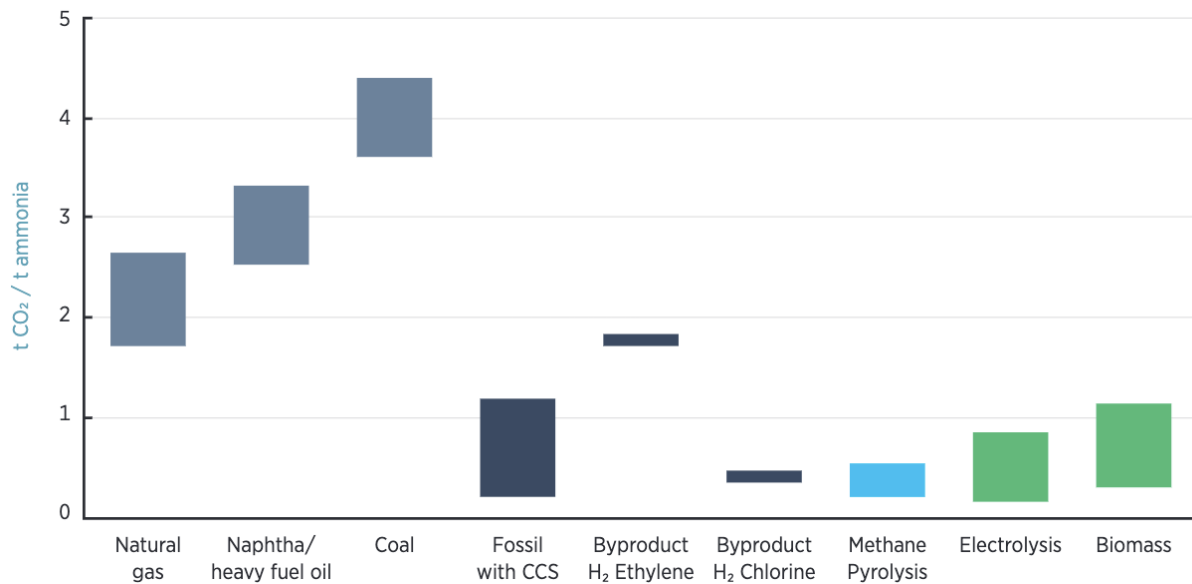


Figure 3.3: Ranges of estimated greenhouse gas emissions of ammonia production from various feedstock [79].

3.1.1 Hydrogen Production

Hydrogen can be produced using renewable- or fossil energy sources, and it can be produced with or without CCS. Based on these factors, hydrogen is categorized as green, blue or gray, with the same requirements as ammonia described in Chapter 3. The two most common methods for producing hydrogen are steam-methane reforming and electrolysis, although alternative methods are also described below in this chapter.

Electrolysis

Electrolysis is a chemical reaction process facilitated by the help of an electric current. The extraction of hydrogen is done when water is split into hydrogen and oxygen by using electricity. The reaction takes place in an electrolyzer that can range in size depending on the intended production scale. Large-scale electrolyzer production facilities can be tied directly to renewable electricity generation. This makes it a promising option for carbon-free hydrogen production. Another possibility is to employ nuclear power for electrolysis, however, this energy source is widely debated due to safety concerns [55].

Water electrolysis for hydrogen production is considered green when coupled with renewable energy sources. However, this process requires 1.6 metric tons of water per tonne of ammonia produced. Additionally, additional water is needed for cooling the ammonia plant, and supporting systems [79].

Reforming and gasification

Reforming is a processing technique in which the molecular structure of a hydrocarbon is rearranged to modify the molecule properties. This technique is commonly used to enhance the combustion characteristics of low-quality gasoline stocks. The by-product of this process is hydrogen [26].

Natural gas reforming is an endothermic reaction which involves methane and steam at high temperatures. The reaction is represented in Equation 3.1 for the process. Hydrogen gas, carbon monoxide and a small amount of CO₂ is created from the reaction. The carbon monoxide can be used further to produce additional hydrogen when reacted with water as shown in Equation 3.2. Natural gas reforming is a widely employed method for hydrogen production and is also the cheapest and most efficient. However, hydrogen produced through this process is classified as gray hydrogen due to the associated CO₂ emissions [58]. Additionally, renewable liquid fuels, such as ethanol, can be used in a reforming process to produce hydrogen [57].



Gasification can be used on feedstocks such as coal or biomass to produce hydrogen. In this process, the coal or biomass is subjected to high-temperature steam and oxygen within a pressurized gasifier, leading to the formation of gaseous components. This process results in a synthesis gas that contains hydrogen and carbon monoxide, which is reacted with the steam to separate hydrogen. Plants used for biomass consume CO₂ from the atmosphere as part of their natural growth process. Utilizing biomass as a gasification feedstock could potentially contribute to a reduction in atmospheric CO₂ levels [57].

Pyrolysis

Methane pyrolysis is a process where hydrogen can be produced from the decomposition of methane [142]. Pyrolysis refers to the heating of organic materials in the absence of oxygen, resulting in the separation of the materials into different molecules [19]. The decomposition of methane through pyrolysis is considered a potential pathway for transitioning from fossil-based to renewable hydrogen production due to its low GHG emissions [124].

The pyrolysis process decomposes methane into hydrogen and solid carbon as shown in Equation 3.3. The carbon is not combusted within this process and there are no CO₂ or other GHG produced. As a result, the pyrolysis process is considered GHG-neutral. The solid carbon produced can be utilized as a raw material for other purposes [142].



Biomass can serve as a viable feedstock for the pyrolysis process as well. The yield of hydrogen obtained from biomass pyrolysis depends on factors such as the type of feedstock, the catalyst used, the temperature and the time of residence [102].

Thermochemical cycles

Thermochemical water splitting is a process where high temperatures from concentrated solar power or waste heat from nuclear power is used to produce hydrogen and oxygen from water. The temperatures involved typically range from 500°- 2000°C, and they drive a series of chemical reactions. The chemicals used in this process are reusable and can be utilized in each cycle. This creates a closed-loop system that only consumes water and produces hydrogen. Thermochemical water splitting is a long-term technology solution with the potential for low or negligible GHG emissions [59].

Comparison of hydrogen production methods

Table 3.1 lists the benefits, drawbacks and the maturity for hydrogen production methods described above.

Table 3.1: Benefits and drawbacks of different hydrogen production methods [102, 92].

Production method	Benefits	Drawbacks	Maturity
Natural gas reforming	<ul style="list-style-type: none"> • Most developed technology • Existing infrastructure 	<ul style="list-style-type: none"> • Carbon byproduct • Dependence on fossil fuels 	Commercial
Methane pyrolysis	<ul style="list-style-type: none"> • Emission-free • Reduced-step procedure 	<ul style="list-style-type: none"> • Carbon byproduct • Dependence on fossil fuels 	Commercial
Biomass pyrolysis	<ul style="list-style-type: none"> • Carbon-neutral emissions • Solid, liquid, and gas product streams • Abundant and cheap feedstock • Developed technology 	<ul style="list-style-type: none"> • Tar formation • Hydrogen yield depends upon the feedstock 	Commercial
Gasification coal	<ul style="list-style-type: none"> • Proven technology • Existing infrastructure. 	<ul style="list-style-type: none"> • Carbon byproduct • Dependence on fossil fuels. • Tar formation 	Commercial
Gasification biomass	<ul style="list-style-type: none"> • Carbon-neutral emissions • Abundant and cheap feedstocks 	<ul style="list-style-type: none"> • Hydrogen yield depends upon the feedstock • Requires oxidation agents 	Commercial
Thermochemical	<ul style="list-style-type: none"> • Oxygen as a byproduct • Zero carbon emissions 	<ul style="list-style-type: none"> • High capital cost • Separation step is required 	R&D
Electrolysis	<ul style="list-style-type: none"> • No pollution with renewable sources • Proven technology • Existing infrastructure • Abundant feedstock 	<ul style="list-style-type: none"> • Low overall efficiency • High capital costs • Energy storage problems • High pressure is required 	Commercial

3.1.2 Air separation

Dry air is primarily composed of three gases; nitrogen, oxygen and argon. The percentage of these gases are approximately 78% , 21% and 1% respectively. This is illustrated in Figure 3.4. Air serves as an excellent source for nitrogen production due to the high percentage of nitrogen gas. Air separation is a process where nitrogen is separated from oxygen in the air. There are three standard methods that is used to separate nitrogen from air; cryogenic distillation, pressure swing adsorption (PSA) and membrane nitrogen generation. These techniques can all be used to produce nitrogen of high purity for industrial applications, such as ammonia production [84].

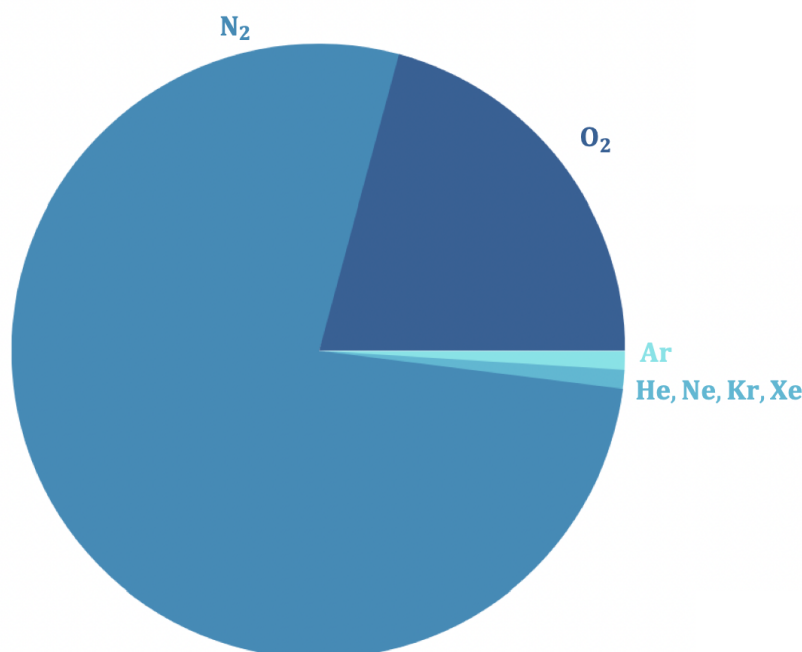


Figure 3.4: Composition of dry air [84].

PSA and membrane nitrogen generation are mechanical processes used to generate nitrogen. These methods exploits the different physical properties of component gases of air to extract the nitrogen. Unlike cryogenic distillation, these mechanical methods are less complex. They depend on the differential speed of travel and adsorption by membranes and molecular sieves to generate nitrogen [64].

The environmental impact of air separation are minimal in terms of emissions. Since the feedstock for nitrogen production is air, the waste gases released from the air separation process are already naturally present in the air. These waste gases normally consist of water vapor, CO_2 and hydrocarbons. The principal impacts of air separation are energy usage for compression, water usage for cooling, use of oil and waste from maintenance [49].

Cryogenic Distillation

Cryogenic air separation is a process in which air is compressed before being cooled to about 10°C and purified by passing it through several filters to eliminate moisture, oil, water vapor, and other contaminants [64]. Cryogenic Distillation produces pure gaseous oxygen and nitrogen, as well as liquid oxygen, liquid nitrogen and liquid argon. This method for separating the air produces high-purity nitrogen. However, it is one of the more complex techniques for extracting nitrogen from air [85].

Pressure Swing Adsorption

PSA is a mechanical nitrogen extraction method. The technology is based on the preferential adsorption and desorption processes to produce nitrogen. Adsorption also called pressurization, removes oxygen, vapor and other impurities from the air, and desorption or depressurization, is a reversal of the absorptive process so that the system is prepared for a new cycle of adsorption. These two process stages are coordinated simultaneously [64].

Membrane Nitrogen Generation

Membrane nitrogen generation is a mechanical method used for extracting nitrogen. Hollow-fiber membranes are used to separate the constituent gases in the air. The surface of the membrane is shaped in a way so that the penetration of the gas is more rapid. Membrane nitrogen generation involves putting atmospheric air into a generator, compressing it and passing the air through several filters before the gas components are separated [64].

Clean compressed air is exposed to the membranes, and parts of the air will flow to the outside of the membrane due to the structure of the membrane fibers. This process is called permeation. The process will remove oxygen, water and some argon until there is only nitrogen left. This is possible because the different molecules have different permeation speeds. Water permeates relatively quickly, while oxygen permeates at a somewhat slower rate but still faster than nitrogen. Nitrogen permeate slowly which means that the nitrogen molecules will remain in the fibers longer than the water and oxygen [35, 64]. After the waste gases has permeated, a nitrogen-rich gas stream is collected [64].

Comparison of air separation methods

Table 3.2 lists the benefits, drawbacks and the abundance for each of the three methods for air separation. The most common method for air separation is cryogenic distillation [139].

Table 3.2: Comparison of air separation methods [139]

Production method	Benefits	Drawbacks	Abundance
Cryogenic Distillation	<ul style="list-style-type: none"> • Low energy consumption • High purity 	<ul style="list-style-type: none"> • High capital cost • Production capacity limitations • Long time start up or shutdown 	Large-scale nitrogen production (80-85%)
	<ul style="list-style-type: none"> • Low capital investment cost 	<ul style="list-style-type: none"> • Large maintenance equipment 	
Pressure Swing	<ul style="list-style-type: none"> • Affordable production 	<ul style="list-style-type: none"> • Noisy operation 	Small-scale nitrogen production (10-15%)
	<ul style="list-style-type: none"> • High purity 	<ul style="list-style-type: none"> • Capacity limitations • Uneconomic for very high purity outputs 	
Membrane	<ul style="list-style-type: none"> • Low capital cost 	<ul style="list-style-type: none"> • Uneconomic for large capacity • High energy consumption per unit nitrogen 	Low-purity nitrogen applications (>5%)
	<ul style="list-style-type: none"> • Flexible product output • Change purity and flow rate 		

3.1.3 Haber Bosch

The Haber-Bosch-method is a process used for the production of ammonia, in which nitrogen from the air reacts with hydrogen, as reaction Equation 3.4 indicates. The Haber-Bosch process, also called synthetic ammonia process, was developed by a German physical chemist named Fritz Haber. Haber was awarded the Noble Prize in chemistry for the method, which made the method economically feasible. Carl Bosch later turned the method into a large-scale process by using a catalyst and high-pressure [27].



The Haber-Bosch process directly combines hydrogen and nitrogen from air under moderate temperatures and high pressures. The use of an iron catalyst allows the reaction to occur at lower temperatures. Extraction of ammonia from the batch as soon as it is formed ensures an equilibrium that favors formation, is maintained. Lower temperature and higher pressure leads to higher ammonia yield in the mixture. The reaction is carried out at temperatures ranging from 400°C to 650°C and pressures from 200 to 400 atm, when used commercially [27].

The process is described in Figure 3.5. The reaction is reversible and the production of ammonia is exothermic. A nitrogen and hydrogen mixture goes into the reactor in the ratio of 1 volume of nitrogen to 3 volumes of hydrogen. In the reactor, the gas mixture is reacted with the catalyst at a specific temperature and pressure before it is cooled so that it turns to liquid. The unreacted gas is recycled, this is because only about 15% of the nitrogen and hydrogen is converted to ammonia each time the gases pass through the reactor. The overall conversion is around 98%, because of the recycling of the unreacted gas [33].

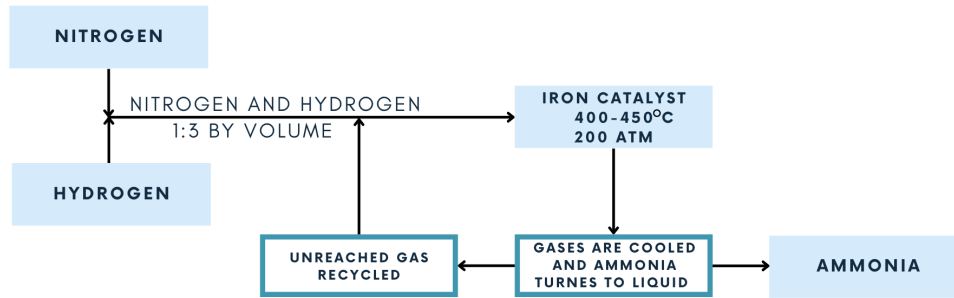


Figure 3.5: Haber-Boch process [33].

3.1.4 Cracking

Cracking is the reverse process of the ammonia synthesis reaction, as Equation 3.5 shows. It involves the separation of ammonia into nitrogen and hydrogen using a catalyst. This process is commonly used where hydrogen is needed as an energy source but is stored and transported in the form of ammonia [1]. The reaction is endothermic and the temperature required depends on the catalyst. Some catalysts require temperatures exceeding 1000°C, while others exhibit high conversion efficiency at temperatures ranging from 650-700°C. These temperatures are well above the operating temperatures for PEM fuel cells, and some of the fuel might need to be burned to maintain an efficient reaction [141, 66].



Figure 3.6 shows a potential design for an ammonia cracking reactor. Ammonia is pumped from a storage tank and passed through a heat exchanger to capture waste heat from the gases exiting the reactor. The preheated gases then proceed through a furnace or catalytic combustor to elevate their temperature to the required level for the reaction. The steam that exits the reaction goes to a separation system which is optimized to produce a very pure stream of hydrogen while leaving enough hydrogen with the nitrogen and ammonia to provide heat for the cracking reaction. This waste gas steam will be combusted to supply heat for the reaction and to remove unreacted ammonia [141].

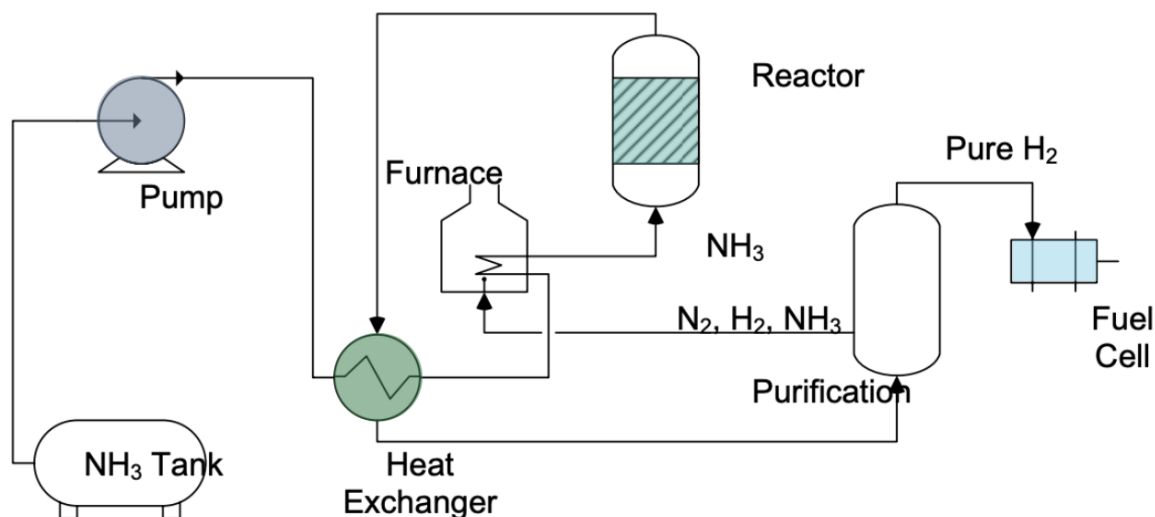


Figure 3.6: Potential cracking reactor design [141].

The thermocatalytic reaction has a theoretical adiabatic efficiency of approximately 85% relative to the energy released from hydrogen. To supply the necessary heat for the reaction without any other available energy sources, more than 15% of the hydrogen would need to be burned. Because of the high temperature needed for the reaction, combustion of ammonia or hydrogen is required onboard if there is no access to other energy sources. PEM cells require a high purity of hydrogen, and less than 0.1 ppm concentrations of ammonia can be present. Not all of the ammonia will be converted to hydrogen, and there are trade-offs between operational costs at high temperatures and the cost of removing the unconverted ammonia [141, 25].

Problems emerge as the temperature in the reactor increases. The materials in the reactor have difficulties to sustain the exposure to this environment which could lead to corrosion. The materials choices are therefore important for a longer lifespan for the reactor. The metal alloy choices become limited and often more expensive for high temperature applications. There will also be required insulation which increases the volume and weight of the reactor. This could increase the time required for the reactor to start producing from a cold state, which is a highly relevant parameter for on-board applications like ships [141].

3.2 Ammonia handling

Ammonia is a well-known hazardous chemical which is transported in larger quantities as goods on ships today. Because of this, there are good, established routines and requirements for storage and handling of ammonia on ships. There have been few reported fatal incidents related to the handling of ammonia by trained personnel [79].

3.2.1 Storage and transportation

Ammonia has been stored and handled for decades by the fertilizer industry. It is transported through pipes, by road, train and on ships. There is already existing infrastructure for significant ammonia trading, with well-established shipping routes and a comprehensive network of ports that handle large amounts of ammonia worldwide [134]. Approximately 25-30 Mt of ammonia are transported each year across the world, with about 18-20 Mt being transported by ships [79]. Russia produces about 3 Mt of ammonia annually, with a significant portion of it transported to various locations globally through pipelines or by ships [78]. The existing infrastructure provides a foundation for the widespread adoption of large-scale transportation of ammonia as an energy carrier and fuel [134].

Ammonia liquefies at a temperature of -33°C or at the pressure of 8.6 bar. Liquefaction of hydrogen involves cooling it to a temperature of -253°C . The process of cooling hydrogen to such low temperatures requires a substantial amount of energy, typically around 20%-30% of the energy content of liquefied hydrogen itself [78].

Ammonia is typically transported in one of three different ways, depending on the storage method used for the cargo. Ammonia is either transported in a semi-refrigerated state at -10°C and 4-5 bar, or it is kept under pressure, typically at 17 bar, when transported in smaller amounts. Large amounts of ammonia are normally stored by refrigeration, typically at -50°C [25]. Large refrigerated ammonia storage facilities are commonly located at ports in close proximity to ammonia production plants [134]. As an indication of scale, the largest tanks for refrigerated ammonia in the world are placed in Qatar. Each of the tanks has a capacity of 50 kt each [78]. Figure 3.7 below shows loading and unloading facilities globally [79].



Figure 3.7: Loading and unloading ammonia facilities on a map of the world [79].

3.2.2 Safety and environmental considerations

There are already safety regulations in place today for handling ammonia, but health risks and environmental risks are emerging as ammonia's role expands. The new systems must be carefully designed to minimize and effectively eliminate these risks. Ammonia are corrosive and potentially toxic and its high vapor pressure under standard conditions enhances the associated risks. However, ammonia has a distinct smell at relatively small concentrations, allowing leakages to be detected before the levels are above long lasting health consequences [134].

The main safety concerns associated with ammonia include its toxicity, flammability and the lowered temperatures [25]. The limits for human exposure to ammonia are defined by legislation and are a function of exposure time and the concentration. The limit is set between 25-50 ppm with dangerous consequences for exposure to concentrations above 300 ppm [71]. It is therefore essential to be able to control all leakage scenarios. This can be done using existing technology for LNG fuels, such as segregation, double barriers in pipes and storage-vessels, leakage detection systems and automatic isolation of leakages [71]. These safety measures are described in Figure 3.8. Ammonia's corrosive nature towards certain materials, such as copper, copper alloys, and zinc, should be carefully considered when selecting appropriate materials for handling and storage systems [25].

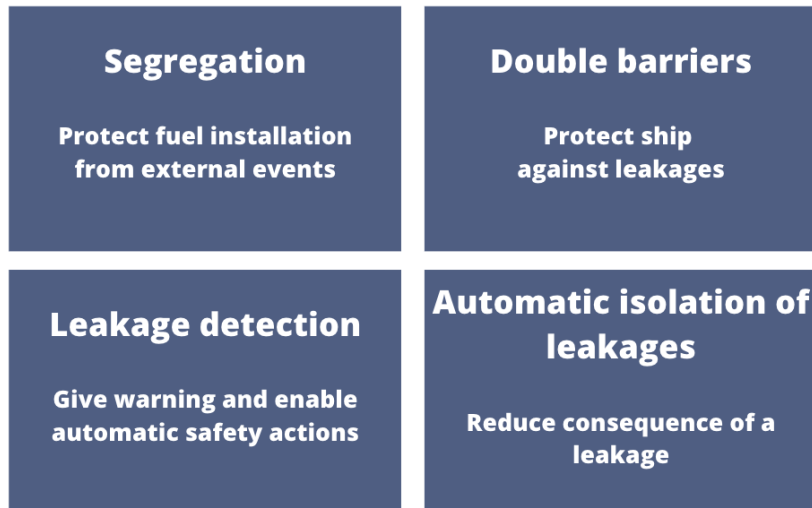


Figure 3.8: Safety measures for ammonia [71].

Ammonia is considered a low-flash-point fuel, requiring a minimum of 8 mJ ignition energy to ignite. In comparison, hydrogen and methane require 0.017 mJ and 0.3 mJ, respectively. The autoignition temperature of ammonia is relatively higher than that of methane. Considerations regarding heat from electrical equipment and explosion protection might therefore be less severe. Additional safety measures should be taken when combining ammonia with other fuels or gases that are more flammable [25].

Spills of ammonia into the sea have an adverse impact on the environment. Ammonia is toxic to aquatic life and can cause long lasting effects on ecosystems. Combustion of ammonia in IC-engines can generate NO_x and also N_2O which are GHG emissions. SCR technology is already available and capable of handling the issue of NO_x . However, engine manufacturers must find a solution to handle N_2O if ammonia is going to be used as a zero emission fuel [71].

3.3 Carbon capture and storage

CCS is a series of technologies that involve the capture, transportation and storage of CO_2 waste from several industries. This technology can cut the CO_2 emissions with more than 90% [154]. The goal of this process is to capture CO_2 in concentrated form, for then to inject it underground. The motivation behind this technology is to reduce CO_2 emissions. The Paris agreement requires the CO_2 emissions to reduce with 50-85% within 2050 [95]. Figure 3.9 illustrates the value chain of CCS. The three stages that complete the entire process will be briefly explained below. There are multiple approaches to carry out this process, and they will be described accordingly, specifically focusing on the hydrogen production outlined in Section 3.1.1.



Figure 3.9: Carbon capture and storage (CCS) value chain [70].

CO_2 capture: There are a broad variety in how CO_2 can be captured. The main focus will be on the process of CCS in combination with blue hydrogen production, which involves the utilization of natural gas. The process that separates CO_2 from natural gas is considered to be the cheapest alternative. Two additional alternatives are to remove it directly from flue gas at power plants for industrial production. It is also possible to capture it directly from the air, direct air capture (DAC), this is the most expensive technology out of these three [111]. For decades, chemical absorption has been used to remove CO_2 from natural gas [30]. As it has been explained in Section 3.1.1, CO_2 is released in the process of creating hydrogen. There is a gas mixture consisting of hydrogen, carbon dioxide and other gasses that can be separated using various methods such as pressure swing absorption (PSA) explained furthered in Section 3.1.2. As mentioned, there are various methods for capturing CO_2 . However, monetary limitations can make it challenging to implement these techniques for every process that emits CO_2 .

CO₂ transport: The transportation of the captured CO₂ is mature. Depending on the distance and quantity being transported, both ships and pipelines can be used. Transport by ship is more suitable for smaller amounts over longer distances [111]. There are more than 6500 km of pipelines dedicated to transporting CO₂ [30]. It is expected that this number will further increase in the future as more projects are being developed.

CO₂ storage: The most secure place to store CO₂ in Norway, is beneath the seabed. The Norwegian continental shelf has a potential for large-scale storage. Ensuring that there are no leaks is of utmost importance when storing CO₂ under the seabed. There is requirements for holding the right pressure and temperature under the seabed to ensure that the CO₂ does not move up, this is achieved under great depths under the seabed. There are several geological formations that allow this [111]. Figure 3.10 illustrates the three steps for CCS. When the CO₂ has been injected under the sea at last, it can be stored there for eternity.

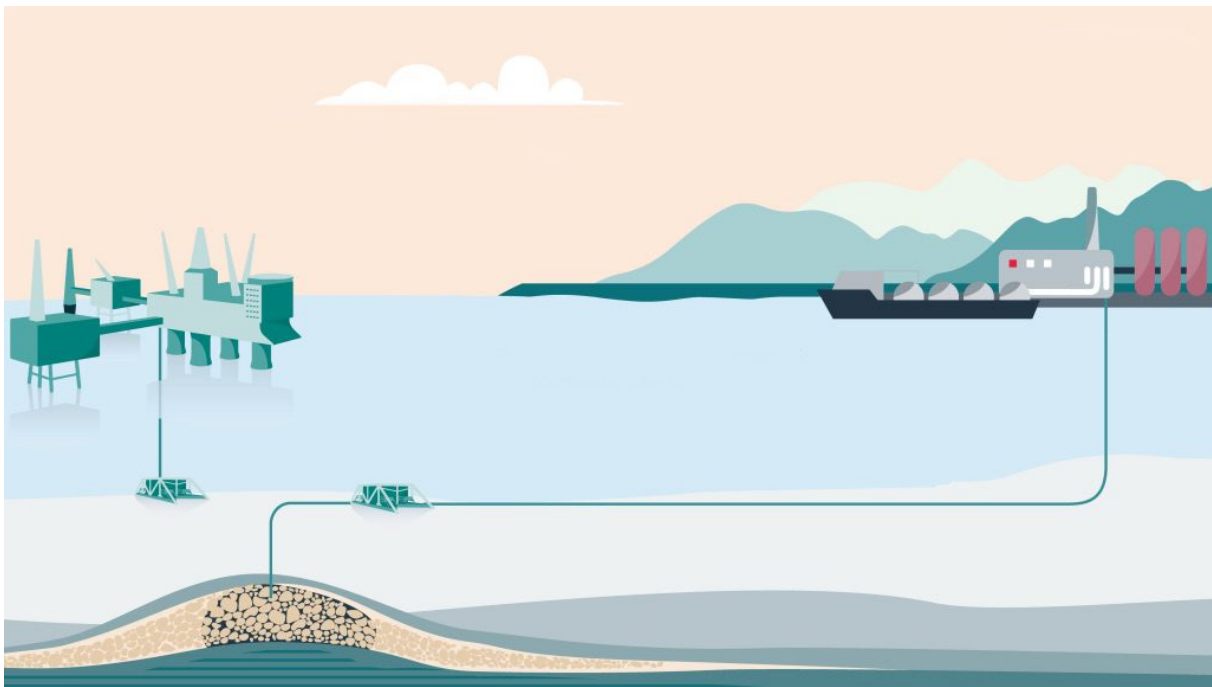


Figure 3.10: Illustration of the process of CCS in three stages [23].

When considering the implementation of CCS, it is important to take into account its disadvantages. The main challenge is the monetary aspect, as industries struggle to make this process cost-effective [2]. An extremely high investment capital is required to afford the pipelines and geological storage resources to complete the process. The potential reward for implementing CCS is not significantly high. This means that firms cannot rely on assured profits from investing in CCS, thereby making it a risky investment [77].

3.4 Current ammonia production and market

Currently, the production of ammonia is predominantly categorized as gray, as depicted in Figure 3.11. Less than 1% of the ammonia produced is derived from renewable energy sources, while around 25% is derived from coal and HFO, and 75% from natural gas and naphtha. The majority of ammonia is primarily utilized as fertilizers, and less than 1% of the ammonia produced are utilized for new applications such as marine fuel, stationary power and as a hydrogen carrier [79].

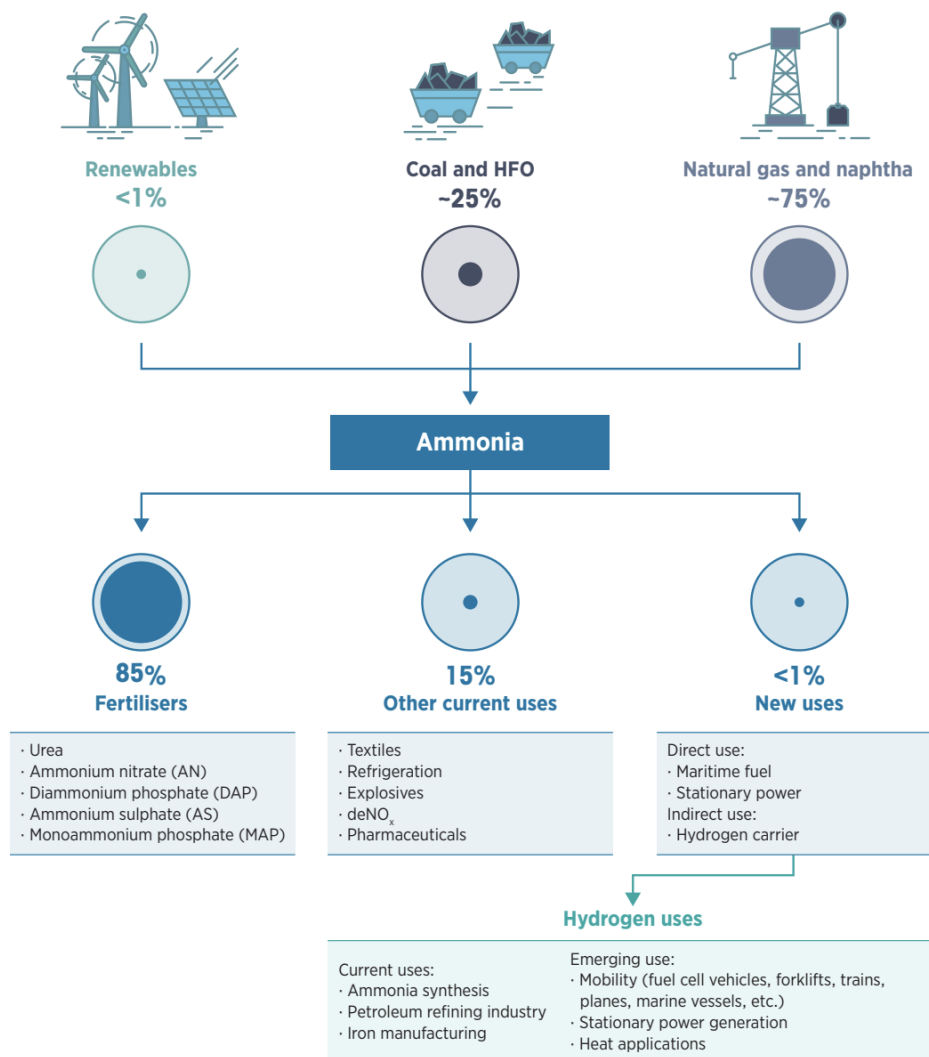


Figure 3.11: Overview of current situation of ammonia utilization and feedstock [79].

Production of ammonia can be separated into the production of hydrogen and the production of nitrogen. Currently, the most commonly used methods for large-scale hydrogen production are natural gas reforming and electrolysis. The natural gas reforming process is considered as a gray ammonia production method, but it can be categorized as blue by applying CCS technology. Hydrogen production by electrolysis is categorized as gray or green based on the energy source used [25].

Nitrogen are most commonly produced through cryogenic distillation due to its cost effectiveness and efficiency. The air separation process generates minimal to no emissions due to the natural content of CO₂ already present in the air, which is released back into the atmosphere. The emissions resulting from the compression process are dependent on the energy sources used to power it [25].

The Haber-Bosch method for producing ammonia is energy efficient, but when fossil feedstocks and fuels are used to power the process, there are significant CO₂ emissions. Around 1% of the total GHG emissions which equals 0.5 Gt of CO₂ are annually caused by fossil-based ammonia production [79]. This number has the opportunity to be reduced by the use of CCS technologies, renewable feedstocks and fuels.

The global production of ammonia was 170 million metric tons in 2018. There was an increase of 44 million metric tons since the year 2000 [25]. Ammonia are produced, stored and shipped around the world. The nation with the largest production is China, accounting for approximately 30% of global ammonia production. This accounts for about 45% of CO₂ emissions tied to ammonia production. The United States, the European Union, India, Russia and the Middle East account for about 8-10% of the ammonia production each. Availability and price of different feedstocks determines the production method. Countries such as the United States and Russia has low-cost natural gas and therefore have natural gas-based plants. China has large coal reserves and uses this as their feedstock for ammonia production [99].

Equinor is a Norwegian energy company primarily active in oil and gas operations. However, in recent years, they have expanded their business to include renewable energy sources and energy storage [143]. Equinor are looking into new, more sustainable opportunities in the maritime fuel market like bio-fuel, methanol and liquid ammonia. The market for ammonia is not sufficient enough today. The current market for ammonia is insufficient. This is due to the reluctance of liquid ammonia-producing companies to scale up production and invest in greener production methods in the absence of competition and an inadequate number of consumers. Potential consumers in the maritime sector, do not want to change their fleets and technologies before there is an well established competitive market for liquid ammonia [106].

Yara is a Norwegian fertilizer and chemical group, which is one of the worlds leading suppliers of mineral fertilizer [3]. They are only producing gray ammonia today, but they want to implement new technologies like CCS, in the near future, to produce blue ammonia. Yara also aims to eventually produce green ammonia on a large scale. However, this goal is projected to be achievable several years in the future [14].

Eidesvik who owns and operates a world-wide fleet of purpose-built vessels announced in 2020 that their supply vessel "Viking Energy" owned by Eidesvik and used by Equinor was to be

modified to run on ammonia [48]. This project is called ShipFC. The project has a five-year time-frame and the project's goal is to be GHG emission free by 2024 when they start operating. Yara is involved in the project and are the main producer of ammonia. Wärtsilä (Wärtsilä Norway), a trading corporation that offers power supply solutions to the marine and energy markets, are responsible for the power technology, storage and distribution systems [147]. Prototech, a company that supplies technical solutions, supported by Fraunhofer IMM, a German research institute, will deliver the ammonia fuel cell system in late 2023 [12, 103].

The price of ammonia is closely linked to the price of natural gas. Between 2000 and 2020, the price of ammonia fluctuated between USD100 and USD600 per tonne. In 2021, the price of ammonia surpassed USD 1,000 per tonne due to natural gas shortages. Table 3.3 shows the energy costs, efficiency and capital costs per tonne ammonia produced by various feedstocks in the US. Production by natural gas are cheaper than by wind which could slow down the process of transitioning to a renewable ammonia production [25].

Table 3.3: Energy costs, efficiency and capital expenditure for various feedstocks for ammonia production [79].

	Natural gas	Coal	Wind
Energy cost (\$/GJ)	3.3	2.1	1.6
Efficiency	66%	44%	52%
Capex (\$/ t_{NH_3})	860	2,063	2,200-3,500

3.5 Future ammonia production and market

Ammonia is currently primarily utilized as fertilizer. However decarbonized ammonia holds the potential to create new markets, including its usage as a fuel in the maritime industry, as a source for power generation and as a hydrogen carrier. Figure 3.12 shows graphically how the demand for ammonia increases in different sectors in the next 30 years. The shipping and hydrogen carrier sectors are expected to experience the largest increase from the present day until 2050. Predictions indicate that by 2050, the market for ammonia as a fuel for maritime transportation and stationary power will surpass the combined size of all current ammonia markets [79].

Figure 3.13 illustrates existing and expanded uses of ammonia. Among the expanded uses of ammonia, there are possibilities for its utilization as a transport fuel [134]. Various consortia have been announced, including the ShipFc project mentioned in Section 3.4, that the first ammonia-fueled vessels are expected to be operating by 2024 or 2025.

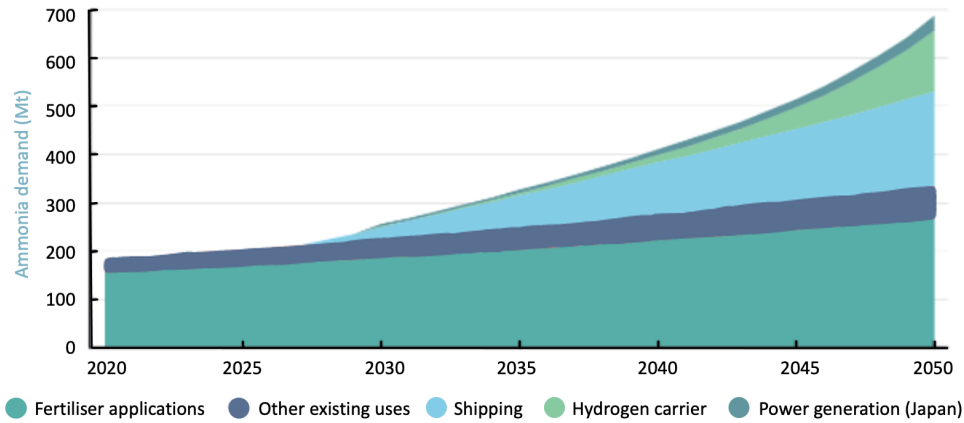


Figure 3.12: Expected demand for ammonia in different utilization categories from 2020-2050 [79].

Ammonia can also be employed as a fuel for electricity generation, either directly or by undergoing cracking processes. It has the potential to displace coal and natural gas as power sources by using gas turbines, furnaces, engines and fuel cells. Ammonia can replace diesel in back-up and off-grid applications by using engines or solid oxide fuel cells. The combustion properties of ammonia can be improved by partial cracking to produce an ammonia-hydrogen blend to increase the combustion properties [79].

The blend of ammonia and hydrogen have been studied by Stefano Frigo and Roberto Gentili, using a four stroke SI-engine with a volume of 505 cm^3 . According to their report presented on the NH₃ Fuel Conference 2014, the additional injection of hydrogen is crucial to enhance ignition and increase the combustion velocity. Furthermore, it is feasible to use alternative pilot fuels like diesel. The ratio of injected hydrogen plays a significant role and varies depending on the load, as it is essential to promote a more stable combustion process [62].

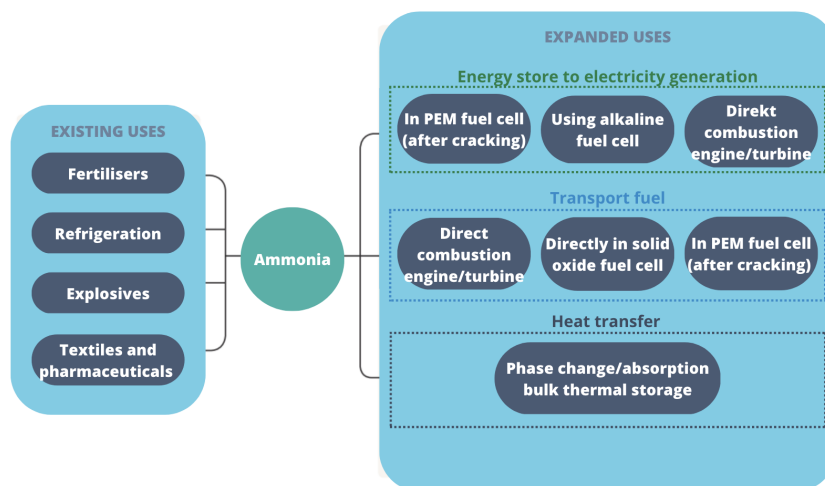


Figure 3.13: Existing and expanded end uses of ammonia [134].

The price of ammonia is closely linked to the gas pricing. A shift towards renewable production feedstock and energy sources could decouple ammonia pricing from the natural gas markets [79]. High gas prices creates an opportunity to make the manufacturing of ammonia cost competitive from 2030 onwards. This can be achieved by a reduction in renewable hydrogen costs, lower renewable electricity production costs, create a higher demand for electrolyzers, removing the risks of new innovative technologies and the creation of a market.

The usage of ammonia is being considered GHG emission free, but the production, storage and transportation of ammonia is not yet without emissions. By using renewable feedstocks and energy sources it would be possible to cut down on the GHG emissions for these processes. Figure 3.14 illustrates the change in feedstock for ammonia production in the next 30 years. It is predicted that most of the ammonia produced by 2050 will be done with renewable energy and CCS technology in a scenario where the Paris Agreement goal of keeping the global temperature rise to below 1.5°C is considered. The transition to renewable energy is predicted to increase the ammonia market to 688 Mt [79].

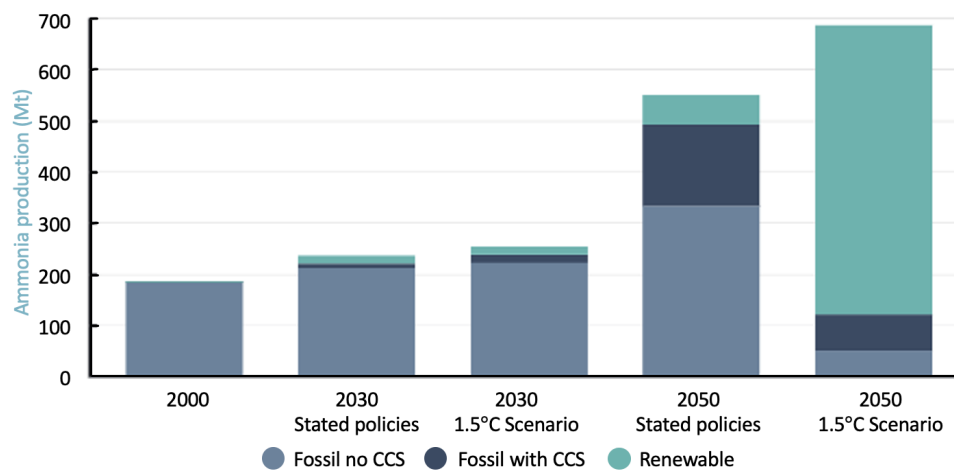


Figure 3.14: Future ammonia production by demand with fossil feedstock, renewable feedstock or fossil feedstock with CCS [79].

3.6 Ammonia in maritime transport

Ammonia as fuel in maritime transport has gained attention in recent years, but the use of ammonia as fuel in the transportation sector, in general, is not a new concept. However, the technology required to power ships with ammonia is still in its early stages of development, and comprehensive advancements and policy measures are necessary for utilization on a larger scale. Several engine manufacturers are currently investigating the challenges associated with burning ammonia in their engines, aiming to make these engines available in the near future. Concurrently, there are ongoing developments in fuel cell technology that utilize ammonia as a fuel source [25]. This chapter will delve into the fundamental principles of combustion engines and fuel cells, highlighting their distinctions and characteristics.

3.6.1 Ammonia for Propulsion Applications

Ammonia can be used as a transportation fuel through direct combustion in an IC-engine or through chemical reactions in a fuel cell to generate electricity. Furthermore, ammonia can be employed as a method of transporting and storing chemical energy, wherein the energy can be released either directly or through the complete or partial decomposition of ammonia to release hydrogen.

The direct utilization of ammonia in a fuel cell or an IC-engine results in substantial enhancements in energy efficiency and decrease energy costs [134]. This chapter will examine the adaptations that can be implemented to incorporate ammonia as a fuel in maritime vessels, with particular emphasis on IC-engines and fuel cells.

IC-engines and ammonia Ammonia as fuel has been explored by researchers since 1822, when it was first applied to locomotive engines [163]. The system utilized the energy of low-pressure ammonia in a fireless engine placed in the locomotive. Inspired by that, ammonia propulsion was tested for street cars in 1872 in New Orleans, USA. Rudolf Diesel worked on an ammonia engine in the 1890s, but after an explosion and serious injuries, he abandoned the idea and went on to invent the diesel engine [25]. During World War 2, Belgium faced a fuel shortage. As a solution, a mixture of ammonia and compressed coal gas was used in 100 vehicles during the winter of 1941-1942, as well as in eight buses starting from 1943. The efficiency was considered comparable to diesel engines before modification [25].

The utilization of clean ammonia as a fuel for IC-engines has been explored and investigated by numerous researchers [121]. Ammonia has a high auto-ignition temperature and low flame velocity. The use of glow plugs to heat the combustion chamber or the use of pilot fuels to initiate the combustion process in both SI- and CI-engines may be necessary [156]. As mentioned in chapter 3.5 on future ammonia, injection of hydrogen or the use of diesel as a pilot fuel can

potentially enhance ignition and combustion velocity.

Ammonia can be combusted in both gaseous and liquid form, as it can liquefy at -33°C . The primarily benefit of directly burning ammonia in an IC-engine is that it can potentially mitigate the need of vessel replacement or costly and extensive modifications [107]. As illustrated in Figure 3.15, the structural composition remains the same, while the combustion process varies.

When ammonia is directly burned in the engine, it results in NO_x emissions. If these emissions occur during regular operation, they can be mitigated through the use of an ammonia catch system. However, the NO_x emissions can also be addressed through the implementation of SCR, which efficiently cleans the exhaust, as mentioned in chapter 2.3.2 [107, 25]. Additionally, it has been suggested that the reduction of NO_x during the expansion stroke of the engine may occur due to ammonia slip [25].

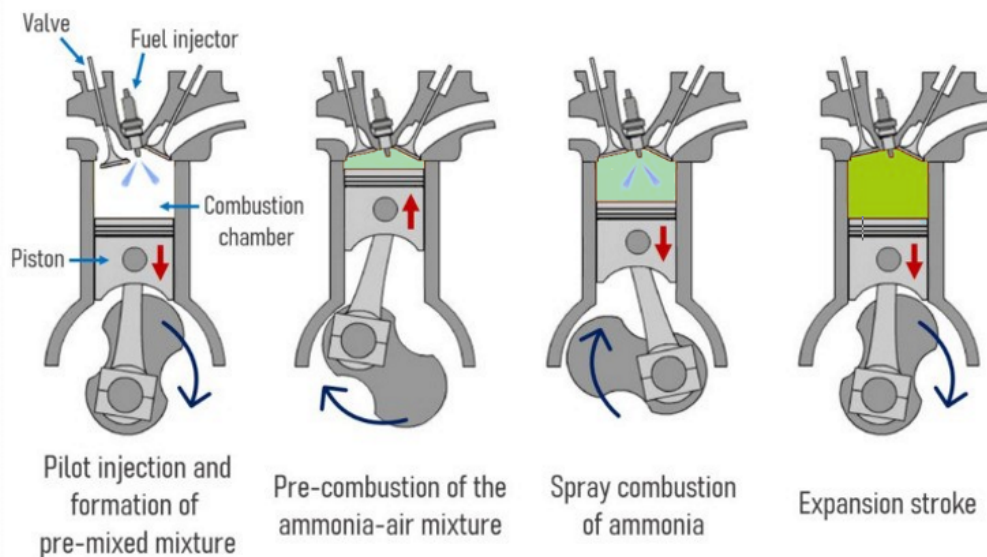


Figure 3.15: Schematic describing the combustion strategy for pure ammonia combustion [31].

Current research and developments

The spacious combustion chamber and longer time scales at low RPM of a two-stroke engine can offer advantages compared to other types of engines [25]. MAN Energy Solutions, a German multinational company headquartered in Augsburg, Germany, specializes in the production of large-bore gas and diesel engines, as well as marine propulsion systems. They are currently in the process of developing a fuel-flexible, two-stroke ammonia engine, positioning it as a leading technology in the maritime energy transition. MAN Energy Solutions aims to have the engine commercially available by 2024, and subsequently introduce a retrofit package for the gradual transformation of existing maritime vessels by 2025 [86].

Regarding four-stroke engines, the technology group Wärtsilä has initiated combustion evaluations involving ammonia. As part of the tests, ammonia was injected into a combustion

research unit to gain a better understanding of its properties. Based on preliminary results, the tests will be continued on both dual-fuel and SI-engines operating on gas [39]. The latest products, such as the Wärtsilä 31, show promise for future adaption of ammonia, whether from diesel, dual-fuel or SI platforms. The Wärtsilä 31 is acknowledged by Guinness World Records as the world's most efficient 4-stroke diesel engine. When planning a marine vessel today, it is beneficial to select a modern engine platform that provides a solid foundation for future fuel conversions [38, 25].

Maritime engine manufacturers anticipate the commercialization of ammonia-fueled two-stroke and four-stroke engines by 2024 or 2025, applicable to both new vessel construction and retrofits [79]. The versatile nature of nitrogen-based fuels enables ammonia to be used within a dual-fuel engine configurations in combinations with diesel, ethanol, gasoline and other options. These features indicate that ammonia can serve as a viable short-term solution that can be implemented in the near future. Dual-fuel engines offer fuel flexibility during the adoption of ammonia as a fuel. It is projected that the first ammonia-powered vessels will begin operations at sea between 2024 and 2025 [79, 31].

Fuel cells and ammonia

Ammonia can be utilized in various types of fuel cells. In fuel cell technologies such as PEMFC, PAFC and MCFC, the ammonia must initially be split into nitrogen and hydrogen, which results in decreased efficiency. Additionally, a significant amount of heat is required to split the ammonia, leading to a portion of the fuel being consumed to generate heat during this process. One drawback of PEMFC is its sensitivity to residual ammonia in the hydrogen supplied to the fuel cell. Due to its lower power output, PEMFC is primarily suitable for propelling smaller vessels like ferries. On the other hand, MCFC and SOFC are considered more suitable for long-distance shipping applications [107, 157]. Figure 3.16 shows how ammonia is used in PEMFCs.

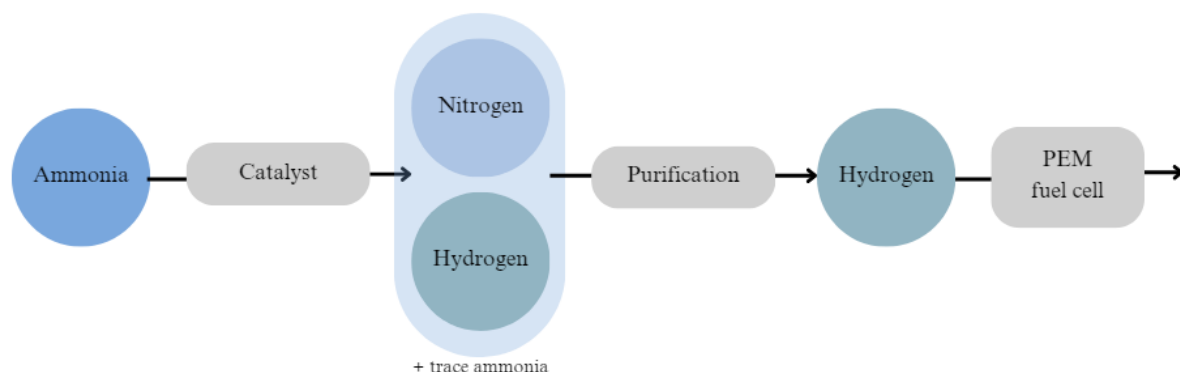


Figure 3.16: Ammonia used in PEM fuel cell [134].

SOFC can directly utilize ammonia as it employs excess heat generated by the fuel cell to split ammonia into hydrogen and nitrogen. Compared to PEMFC, SOFC offers higher efficiency and even has the potential to surpass the efficiency of two-stroke engines [79]. Unlike internal combustion engine, there is no need to handle exhaust gases with SOFC, as it produces zero emissions of particulates or NO_x . The utilization of ammonia in SOFC is feasible due to the decomposition of ammonia at high operating temperatures [107, 156].

4 Case maritime fuel comparison

This case aims to evaluate the possibility of implementing blue ammonia as a marine fuel, in the areas of cost, emissions and efficiency. The case study will compare HFO, blue ammonia and biodiesel in a life cycle analyses, using tools such as MATLAB and SimaPro. The foundation for comparison is based on an already existing route between Mongstad and Reykjavik, traveled by an oil/chemical tanker named Fure Valö. This exciting route and vessel will also serve as background for many of the design choices and constraints for the case study.

Ammonia is considered a CO₂ neutral fuel since no CO₂ is emitted during combustion. However, there are significant amounts of NO_x emitted during utilization. In addition to this, emissions from the production and transport processes of blue ammonia contribute to other GHG emissions. The overall environmental footprint from production to combustion is what is being accounted for, when evaluating blue ammonia as a future marine fuel. Further, it will be important to investigate the costs and efficiency associated to blue ammonia, to fully assess its feasibility for implementation in the fuel market.

4.1 Technological aspects and design

The technology used for the case are already existing, or will be in the near future. For comparison purpose, the design choices and constraints concerning the vessel remain universal. This section reflects on the decisions made for this case study, in terms of fuel, engine and vessel choices.

4.1.1 Fuels

This case compares the fuels HFO, blue ammonia and biodiesel. HFO are used in this case for reference with intention to be compared to the sustainable new options such as ammonia and biodiesel. Table 2.1 in Chapter 2.1 compares the energy density and emissions for different fuels, and has been a guidance for deciding fuels to compare liquid ammonia with.

HFO is widely used in maritime transport today. The energy density for this fuel is found in Table 2.1 are 35 *MJ/L*. This high energy density per liter in combination with its accessibility and cost are the main reasons it has been used for several decades, as described in Chapter 2.1.

Technologies like scrubbers, SCR and CCS on-board written about in Section 2.3.2 show possible improvements when using fossil fuels like HFO, and have the ability to significantly improve the total environmental footprint. The reason why these scenarios are not taken into consideration during the case, is that HFO without improvements is used as a reference for comparison. There are however, regulations that implement that these types of technologies will be necessary in the future if HFO is something the maritime sector wants to continue using.

The chosen biodiesel for this case is B100, which represents a 100% pure bio-blend typically produced from vegetable oils or animal fats. Biodiesel meets the overall requirements for biofuels and the standard for renewable fuels [53]. While HFO is used as a reference, biodiesel and blue ammonia are considered fuels for the future. Biodiesel is selected as an alternative fuel for comparison based on its significant potential for emission reduction. In fact, biodiesel has been found to produce 74% less GHG emissions than petroleum diesel [133]. However, one issue related to sources such as biofuels, is that they can come in conflict with other sectors such as the food sector, shortly explained in Section 2.1. Besides that, biodiesel should be considered as an option as a future fuel to gain a better understanding on which alternative can be considered to be the best. There are also withdraws related to biodiesel that will be taken into consideration.

The current production method and market for ammonia were taken into consideration when selecting the type of ammonia for the case. While green ammonia might seem like the obvious choice in terms of GHG emissions, it is important to note that ammonia produced from natural gas offers the advantage of lower capital expenditure like Table 3.3 in Chapter 3.4 shows. The production of ammonia is expected to predominantly rely mostly on fossil fuels, either with or without CCS in the next 30 year as Figure 3.14 in Chapter 3.4 illustrates. Therefore the choice of blue ammonia produced with steam gas reforming and with CCS was chosen for the case.

Table 4.1 give an overview of some important properties with each of the fuel.

Table 4.1: Important properties to give a foundation for comparison.

Fuel	Energy density (MJ/kg)	Densety kg/m ³
HFO	40.5	1,000 [138]
Biodiesel	37.8	875 [63]
Ammonia	18.6	682 [67]

4.1.2 Vessel and engine

Fure Valö is a chemical/oil tanker and is as mentioned currently traveling the distance from Mongstad in Norway to Reykjavik in Iceland. Its gross tonnage is 12770 tons and dead-weight tonnage is 17991 tons. The info in appendix B.1 presents the technical documentation of the ship. Since these vessels are created to carry pressurized, liquefied gas, they are equipped with insulated stainless steel fuel tanks on deck that can be used to store ammonia [96].

When deciding on which propulsion system to use for the ship it is important to look at the distance, weight and the amount of power that is needed for the vessel. As mentioned in chapter 3.6.1 and 3.6.1, there is several systems that can run on ammonia. Traditional IC-engines remain the prevailing choice in the maritime sector today due to their economic viability. As fuel cells are not yet commercially available, their cost remains high, making IC-engines the most cost-

effective option currently [25]. The ship Fure Valö is already installed with a dual-fuel engine that makes implementation of ammonia as a fuel smoother, cost-efficient, and easily put into effect within a reasonable future [31].

Fure Valö is equipped with the dual-fuel engine Wärtsilä 9L34DF, which is a medium-speed four-stroke combustion engine. This motor is in the mid-range of the Wärtsilä 4-stroke multi-fuel engine collection for main engines. Dual-fuel means that it can operate the vessel on LNG or traditional liquid marine fuels such as LFO, HFO or biodiesel. Fuel switching happens smoothly without loss of power or velocity. This gives the option to select fuel according to cost and availability. A great advantage is that it can operate on low-emission fuel when sailing in emission control areas (ECAs). The rated power at 500 kW/cyl and 750 rpm is 4,500 kW [37]. In Figure 4.1 and Table 4.2 the motor and dimensions are presented.

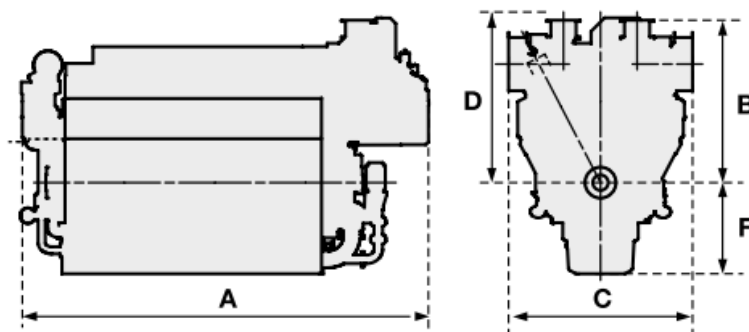


Figure 4.1: dual-fuel engine Wärtsilä 9L34DF [37].

Table 4.2: Engine dimensions (mm) and weight (metric tons) [37].

9L34DF	A	B	C	D	E	Weight
	6,796	2,423	2,609	2,345	1,153	49

When ammonia is burned directly in the engine it will produce NO_x . The NO_x emissions can be handled using SCR technology as mentioned in 3.6.1. Wärtsilä has developed an after-treatment system based on SCR called Wärtsilä NO_x Reducer (NOR). NOR, which is optimized and validated for Wärtsilä medium-speed engines such as the 9L34DF used in this particular case, offers various advantages in terms of reliability, flexibility, size, and easy installation and maintenance onboard the ship [150]. The size of NOR is optimized in terms of modularity, performance and costs. The typical NO_x emission reduction is 90 % [40].

The product also works very well in combination with any of Wärtsilä's scrubbing systems. In tests done by Wärtsilä, sulphur dioxide removal efficiency are exceeding 99% in all operating conditions, even when using high sulphur fuel [149].

Tier II and III are emission standards for new engines and was introduced by IMO in 2010. Tier II limits are global, while Tier III standards apply only in NO_x Emission Control Areas.

NO_x emission limits are established for diesel engines based on their maximum operating speed [105, 42]. According to Wärtsilä, the 34DF engine is compliant with Tier II standards when operating in diesel mode and Tier III standards when operating in gas mode. Additionally, when integrated with NOR, Tier III compliance can also be achieved in diesel mode [37].

Since the dual-fuel engine can operate on LNG, and the existing technology is already in use as mentioned in chapter 3.2.1, the same technology can be used for ammonia. In Figure 4.2, it is illustrated an example of installation of ammonia on the ship.

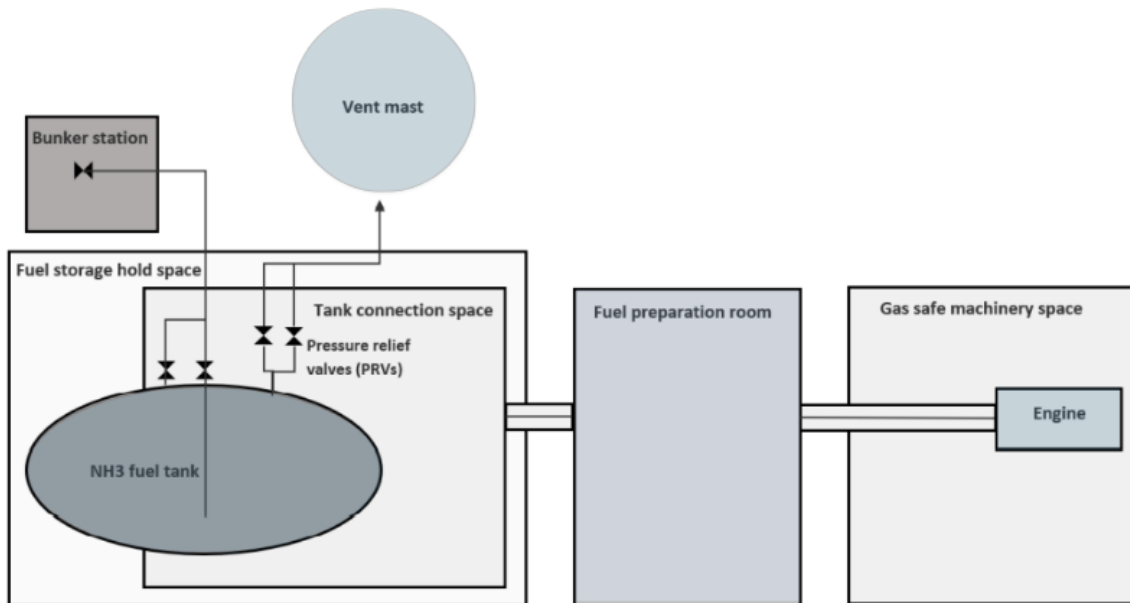


Figure 4.2: With implementation of ammonia on ships, the general arrangement in regards to engines and fuel storage is affected by the installation. The figure shows a diagram of how it could look with ammonia installed on-board with safety barriers [71].

4.2 Route and distances

Yara is the leading producer of ammonia in Norway, it is therefore assumed that one of their locations is where the ammonia will be produced [3]. Yara's ammonia production plant is located in Porsgrunn, this location is therefore chosen as the production site for the liquid ammonia [3]. Mongstad refinery has the means to produce biodiesel. They have tested a mix of 30% biodiesel and 70% MGO between Mongstad, Norway and Reykjavik, Iceland. This blend showed promising performance results [126]. This project gave the foundation for choice of route. All fuels will be utilized in a chemical/oil tanker described in Chapter 4.1.2, transporting it the distance of 1,000 NM. For simplifying reasons, it is assumed that Mongstad refinery has the means to produce HFO, since it can produce fossil based fuels.

It has also been made an estimate of the route to be 1,000 NM, since this assure that there will be enough fuel to cover the distance of 941 NM between the two ports [114]. The reason why

this specific route was chosen for the case is that this route is already utilized by Fure Valö. The distance of 1,000 NM is considered to be a middle-length route, making it a suitable distance for comparing the performance of different fuels.

The ammonia will be transported by trucks from Porsgrunn to Mongstad, which is a distance of 437 km one way [90]. When the right amount of fuel has arrived in Mongstad, the ship will be fueled up, and the journey between Mongstad and Reykjavik can begin. Figure 4.3 provides an overview of the transportation distances utilized in the case study, illustrating the various distances involved. The fact that HFO and biodiesel is produced at the delivery site gives them an advantage that will have to be taken into account. To further figure out how many times the trucks will have to drive the given distance, the required amount of ammonia as fuel to complete the distance of 1,000 NM, will have to be calculated.



Figure 4.3: Ammonia is transported by truck from Porsgrunn to Mongstad, both in Norway. All three fuels are utilized in a oil/chemical tanker from the delivery site in Mongstad to Reykjavik, Iceland.

4.2.1 Fuel required

In order to calculate the required amount of each fuel to cover the distance, it is important to have knowledge about the energy density that can be delivered. Table 2.1 holds this information. The supply energy for ammonia, HFO and biodiesel is 18.6, 40.5 and 37.8 MJ/kg respectively.

This indicates that a larger quantity of ammonia needs to be transported in order to provide sufficient fuel coverage for a distance of 1,000 NM. The average speed provided by the vessel is 10.6 knots, shown in appendix B. It will take the vessel approximately four days to complete the journey between Mongstad and Reykjavik. These calculations have been based on Equation 4.1 below, where the values are based on the distance of 1,000 NM, and average speed of 10.6 knots, converted into meters, and meter per second, respectively. Appendix C displays that it would take the vessel 94 hours to complete the journey.

$$\begin{aligned}
 t_{ship} &= \frac{\frac{d_{ship}}{s_{ship}}}{3600s/h} \\
 d_{ship} &= d_{NM} \cdot d_m \\
 s_{ship} &= s_{knots} \cdot s_{m/s}
 \end{aligned}
 \tag{4.1}$$

Appendix B holds dimensions and information about the vessel Fure Valö chosen for this case. This information has been compared with other vessel types called handysize ships, which holds similar dimensions and speed. These ships consume around 25 metric tons of fuel per day. Given that it takes the vessel four days to complete the journey, it is assumed that the consumption of 100 metric tons of HFO is required to cover this distance [160, 146].

To determine the required amount of the two other fuels, Equation 4.2 has been used to complete the calculations. Table 4.3 show that the amount of ammonia and biodiesel required is 217.7, and 107.1 metric tons respectively. These calculations have been based on the energy density each fuel can deliver shown in Table 4.1. These calculations clearly demonstrate that ammonia is the least efficient fuel among the three options, as it requires more than double the amount compared to the other fuels to cover the same distance.

$$m_{fuel} = \frac{m_{HFO} \cdot SE_{HFO}}{SE_x}
 \tag{4.2}$$

Table 4.3: Fuel required.

	Fuel required (kg)
Ammonia	217,742
Biodiesel	107,143
HFO	100,000

As mentioned above, ammonia will be transported from Porsgrunn to Mongstad. It is assumed that these trucks are provided by Yara. The trucks supplied holds a capacity of 11,000 gallons, which is equivalent to 41.6 m^3 . This information is used to determine the number of truck rides required to transport the ammonia from the production site to delivery. Table 4.1 shows the

density of each fuel and the amount required of each fuel is collected from Table 4.3. Equation 4.3 shows how the calculations of how many trucks are required to transport ammonia. There will be a total demand of eight trucks to transport the ammonia as seen in appendix C. Table 4.1 displays that ammonia has a lower density compared to the other two fuels, resulting in a larger volume requirement. Consequently, ammonia can be considered the least efficient fuel in terms of volume and energy delivery.

$$\begin{aligned}
 n_{truck} &= \frac{V_{fuel}}{V_{truck}} \\
 V_{fuel} &= \frac{m_{fuel}}{\rho_{fuel}}
 \end{aligned}
 \tag{4.3}$$

It is assumed that all eighth trucks will return to the starting point which is the production site. This means that there will be eight round trips in total. The distance of 437 km will then be covered 16 times, resulting in a total distance of 6,992 km. The fuel consumption of the truck is assumed to be 0.25 kg diesel per km [43]. Equation 4.4 has been used to determine the required diesel amount, which is 1,748 kg of diesel. These additional costs and emissions caused by diesel consumption are attributed solely to ammonia.

$$\begin{aligned}
 m_{diesel} &= m_{diesel} \cdot d_{truck_{tot}} \\
 m_{diesel} &= 1,748kg
 \end{aligned}
 \tag{4.4}$$

4.3 Life cycle assessment

LCA can be utilized as a tool to assess the environmental impact of various products and processes. Cost and efficiency are important factors that are taken into consideration throughout the case study. This LCA will consider the environmental impact of the fuels. The finalized results obtained from this will be evaluated together with cost and efficiency to gain a comprehensive understanding of the overall impact of blue ammonia as a fuel. It is important to note that HFO and biofuels are used as base for comparison. The interpretation phase of this LCA will further be discussed in Section 5.

4.3.1 Goal and scope

Goal: The goal of this LCA is to compare the life cycle impacts of each of the three fuels. This can help provide valuable insights into identifying the better alternative fuel option, thereby expediting the process of decarbonization in the maritime sector.

Scope: The functional unit for this LCA will be emissions per kg. It will essentially be a cradle-to-grave system boundary. Similar or unnecessary components are removed. This case study will focus solely on the LCA of different fuels and will not consider emissions associated with the ship itself. This is illustrated in Figure 4.4. It is assumed that the power plant has the capacity to produce ammonia, and the refinery has the capacity to produce HFO and biodiesel. Therefore, emissions related to manufacturing are not considered in this case study.

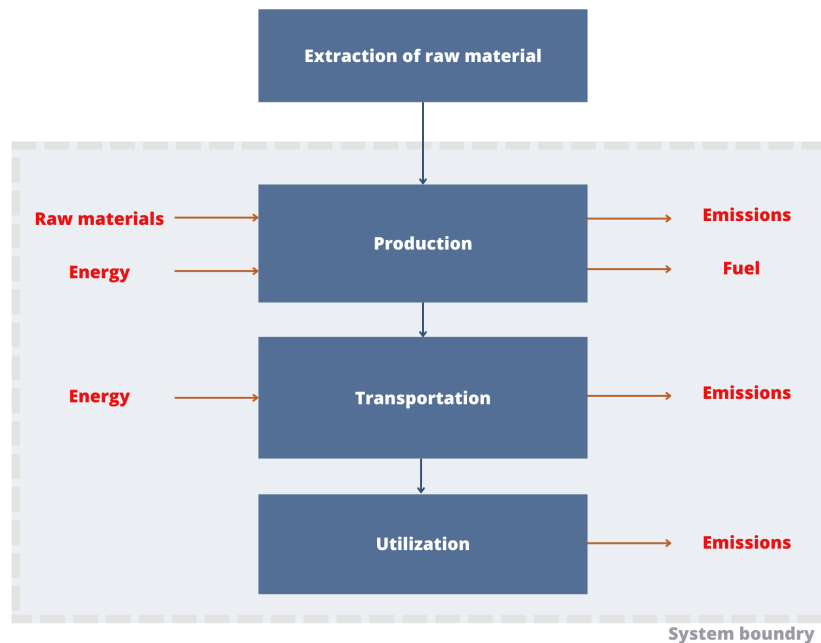


Figure 4.4: System boundary that defines the LCA.

4.3.2 Life cycle inventory

The SimaPro software has been utilized as a tool to compare the emissions associated with the life cycle of each fuel. Certain parts have been excluded due to similar processes, such as extraction of raw materials for ammonia and HFO, as well as the limited availability of data. The global warming potential (GWP) will carry the most weight in the comparison, along with other significant factors such as acidification and human toxicity.

This LCA is based on simplifications and available data. It is assumed that the HFO used does not have any emission reduction technologies, such as scrubbers to remove NO_x and SO_x , nor does it include any CCS on-board. The reason for this is that the HFO commonly used so far, does not include these improvement measures. Therefore, the comparison will be based on an unimproved HFO as the reference.

Sections 4.2 and 4.2.1 provide an explanation that reveals the need for more than double the amount of ammonia compared to HFO and biodiesel to cover the same distance. There will

also be emissions associated with the transportation of ammonia from Porsgrunn to Mongstad, which initially puts ammonia at a disadvantage compared to other fuels.

The data used in this study has been collected from various LCAs, resulting in a wide range of values due to differences in process efficiency and material quality. The inventory lists below, gives an indication of which inputs are used to complete the LCA. Many of the results presented in this study are based on mean values. There has also been done conversions of values, to provide suitable units for comparison.

To align HFO with the processes in SimaPro and ensure compatibility with available data, certain adjustments have been made to create a standardized unit of one kg of HFO. These adjustments enable accurate comparisons and consistent assessment within SimaPro. The inventory list presented in Table 4.4 below is the outcome of these adjustments. In addition to considering the inputs required for HFO production, the emissions during combustion have also been taken into account. This is shown in Table 4.9. By including these additional processes, enough valuable inputs have been provided to conduct an LCA of HFO for comparison.

Table 4.4: Inventory list for producing 1 kg HFO [82].

Material	Amount	Unit
Inputs		
Water	0.2	kg
Brown coal	3.28	g
Hard coal	4.03	g
Crude oil	0.97	kg
Natural gas	0.05	kg
Electricity	0.056	MJ
Outputs		
Heavy fuel oil	1	kg
CO ₂	0.27	kg
NO _x	0.00077	kg
CH ₄	0.003	kg
SO _x	0.0016	kg

There are several processes tied to the production of blue ammonia. These can be seen in the inventory lists in Table 4.5, 4.6 and 4.7. Hydrogen and nitrogen are produced separately, before they are combined using Haber-bosh seen in Table 4.7. If Hydrogen was to be produced without CCS, it can be expected to be CO₂ emissions of around 9.3 kg per kg hydrogen produced [120].

A simplified version of CCS has been implemented in the hydrogen production. As mentioned in Section 3.3, 90% of CO₂ emissions can be reduced. The removal of 90% CO₂ has been considered, as it is of relevance for the fuel. No energy or materials required for the implementation of CCS have been included in the assessment. Table 4.5 holds the inputs required to produce 1 kg of blue hydrogen.

Table 4.5: Inventory list for producing 1 kg of blue hydrogen [162].

Material	Amount	Unit
Inputs		
Natural gas	3.5	kg
Electricity	1.13	MJ
Steam	18.8	kg
Outputs		
Hydrogen	1	kg
CCS (CO ₂)	-8.4	kg
CO ₂	4	kg
NO _x	3.21	g
SO _x	1	g
PM	63.9	g

Table 4.6 shows the inputs that are needed to produce 1 kg of nitrogen. This is based on information about cryogenic air separation in Section 3.1.2, and available data. Adjustments have been made to ensure that the inputs align with the production of 1 kg of nitrogen, as it is used as the functional unit for comparison.

Table 4.6: Inventory list for producing 1 kg of nitrogen [7].

Material	Amount	Unit
Inputs		
Air	1.29	kg
Electricity	4.03	kWh
Water	3.48	kg
Outputs		
Nitrogen	1	kg

Lastly, the inventory list for the production of blue ammonia is presented in Table 4.7 below. The processes of producing hydrogen and nitrogen are now combined, and ammonia is produced. An Norwegian energy mix has been used in SimaPro. The emissions from combustion have been taken into account when developing the life cycle of ammonia. Since ammonia is a zero-carbon fuel during combustion, only NO_x emissions are considered in Table 4.9. Additionally, a process has been included to account for the emissions associated with the transportation of ammonia. The diesel trucks have to cover a total distance of 6,992 km, which corresponds to the total transportation distance of ammonia. This has been added to complete the life cycle of ammonia.

Table 4.7: Inventory list for producing 1 kg of blue ammonia with Haber-Bosch [17].

Material	Amount	Unit
Inputs		
Blue Hydrogen	0.177	kg
Nitrogen	0.823	kg
Electricity	2	kWh
Outputs		
Ammonia	1	kg

There has also been made an inventory list for production of B100. Since the biomass used in production is used vegetable cooking oil, the extraction of raw materials is not considered since it can be seen as a recycling process. There are some inputs of fossil-based materials involved in the production of biodiesel, similar to ammonia and HFO production. The extraction of raw materials is therefore completely neglected as it is not relevant to the comparison of the fuels. There is however, emissions tied to the combustion of biodiesel, these are shown in Table 4.9, and have been considered in the LCA.

Table 4.8: Inventory list for producing 1 kg of biodiesel [140].

Material	Amount	Unit
Inputs		
Water	0.088	kg
Methanol	0.241	kg
Sulphuric acid	0.011	kg
Potassium hydroxide	0.014	kg
Diesel	0.024	kg
Used vegetable cooking oil	1.129	kg
Electricity	0.481	MJ
Outputs		
Biodiesel	1	kg

Table 4.9 provides an overview of key emissions resulting from the combustion of each fuel. The most relevant emissions for comparison are CO_2 , NO_x and SO_x . These numbers have been put together with the required amount of each fuel. The emissions of SO_x are negligible [34].

$$m_{\text{emission}} = m_{\text{emissions}} \cdot m_{\text{fuel}} \quad (4.5)$$

Table 4.9: Emissions for combustion of the fuels in kg/kg fuel.

Emission	Unit	Ammonia	Biodiesel	HFO
CO_2	kg CO_2 /kg fuel	-	2.86 [36]	3.1 [6]
NO_x	kg NO_x /kg fuel	0.47 [11]	0.048 [151]	0.14 [6]
SO_x	kg SO_x /kg fuel	-	-	0.2 [6]

4.3.3 Life cycle impact assessment

The following section will present the results based on the data collected in Section 4.3.2 above. There main focus will be on the emissions associated with the production and utilization of the fuels. Programs such as SimaPro and Matlab have been used as tools to illustrate the impacts. This provides insight into how each fuel affects multiple categories within the chosen system boundary of this LCA. Some key emissions that are further examined include CO_2 , SO_x and NO_x emissions.

There are several impact categories to consider when conducting an LCA. Table 4.10 below provides an explanation of selected impact categories deemed suitable for this LCA, specifically in the context of comparing three fuels used in the maritime sector.

Table 4.10: Suitable impact categories to consider in the comparative LCA between the three fuels - explanation [73].

	Description	Unit
Global warming	This is used to measure the potential contribution of the fuels to climate change in the form of emissions of greenhouse gasses, specifically CO_2 and N_2O	kg CO_2 -eq
Ozone layer depletion	Used as an indicator of how the emissions to the air cause destruction to the ozone layer emissions such as nitrogen oxides, chlorofluorocarbons and methane	kg CFC-11-eq
Human toxicity	Measures the potential human health impacts that are associated with the production, use, and disposal of the fuels. This looks at the exposure to toxic substances and associated pollutants emitted to the enviroment	kg 1,4-DB eq
Ecotoxicity	The impact on the health and well-being of nonhuman species and ecosystems through production use and disposal of the fuels Spesifically considering the marine aquatic ecotocity	kg 1,4-DB eq
Acidification	The contribution of emissions of nitrogen oxides (NO_x) and sulfur dioxide (S_2O) and measure the potential for them to lead to acid rain and other forms of environmental impacts caused by acidification	kg SO_2 -eq
Eutrophication	Considers the emissions of nitrogen and phosphorus and how they may contribute to excessive growth of algae and other aquatic plants	kg PO_4 -eq

Figure 4.5 compares the three fuels through their life cycle. It provides a solid indication of the impact each fuel has on multiple categories. The graph illustrates significantly lower emissions from ammonia compared to HFO and biodiesel within the Global Warming Potential. There are, however, other factors that need to be considered, where the impact of ammonia is worse.

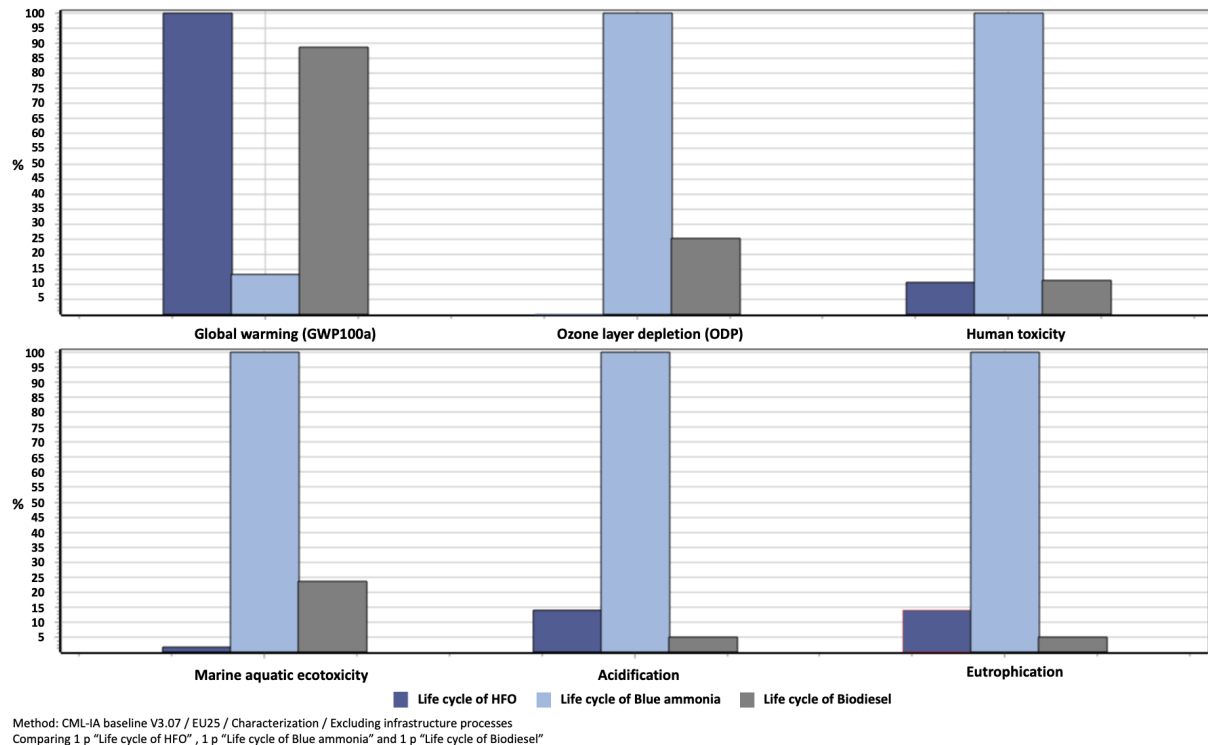


Figure 4.5: Simapro has been used as a tool to illustrate the comparison between the fuels., The x-axis include the impact categories for consideration, while the impact of each fuel is displayed in percentage on the y-axis.

Table 4.11 which corresponds to Figure 4.5, presents the quantities of each impact category along with their respective units. There is a significant variation in the impact category that has the most significant effect on the environment.

Table 4.11: This table belongs with Figure 4.5, and holds the data of the different amounts of each impact category for the three fuels.

Impact category	Unit	Ammonia	HFO	Biodiesel
Global warming	kg CO_2 eq	4.87e+4	3.664e+5	3.25e+5
Ozone layer depletion	kg CFC-11 eq	2.65e-3	1.05e-6	6.75e-4
Human toxicity	kg 1.4-DB eq	1.6e+5	1.71e+4	1.85e+4
Marine aquatic ecotoxicity	kg 1.4-DB eq	7.09e+7	1.1e+6	1.68e+7
Acidification	kg SO_2 eq	5.08e+4	7.12e+3	2.61e+3
Eutrophication	kg PO_4 -eq	1.32e+4	1.83e+3	6.73e+2

Figure 4.6, utilizing Table 4.9 shows how the combustion of each fuel affects the key emissions. This has been based on the required amount of each fuel to transport the ship from port to port, making it 1,000 NM. This has been multiplied with the amount of emissions per kg of combusting each fuel, and can be seen in Equation 4.5.

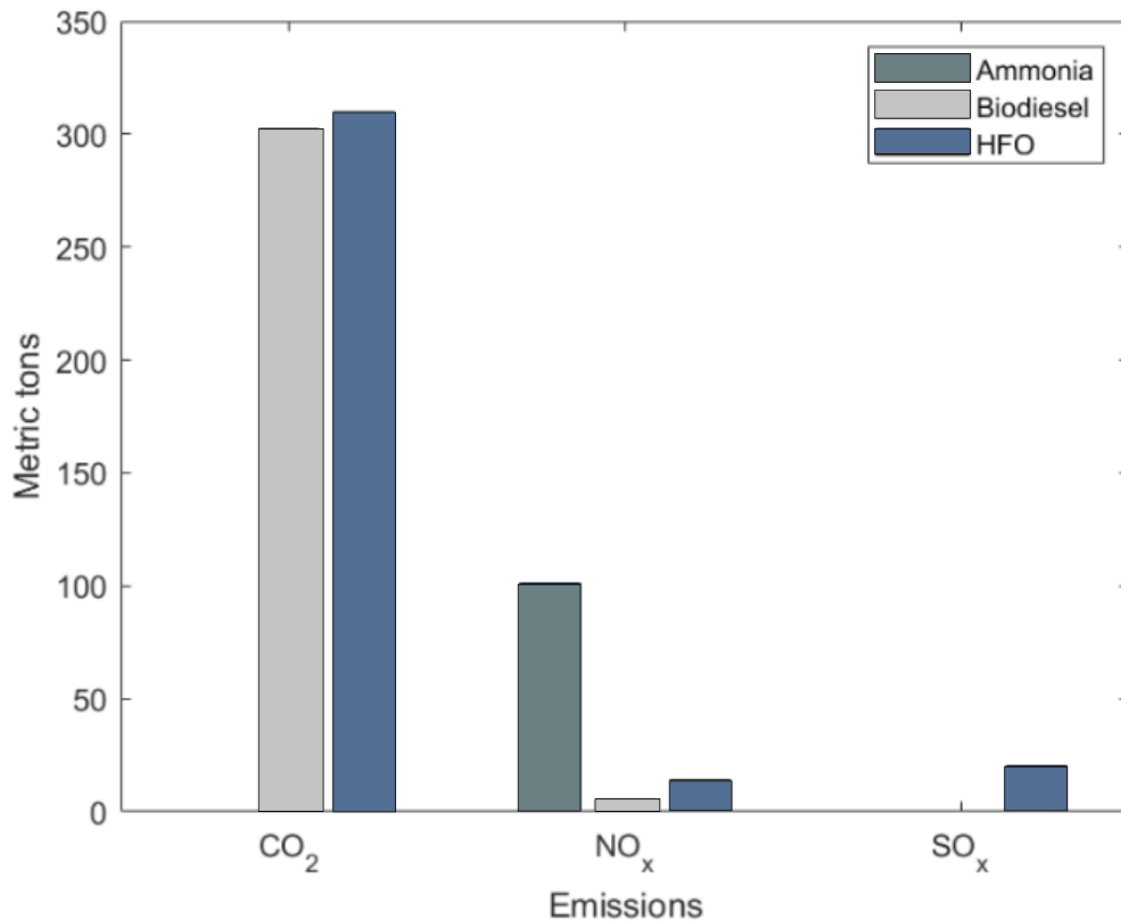


Figure 4.6: Each of the three fuels affect the environment with different emissions through the combustion when utilized as fuels. This shows how some key emissions disturb the environment when utilized a distance of 1,000 NM.

Examining the LCA of ammonia alone reveals the components that have the most significant impact on various categories. Figure 4.7 shows which components affect the different impact categories the most through production, transportation and combustion of ammonia as fuel. The impact of production and utilization varies significantly across different categories, while transportation has a relatively minor overall impact.

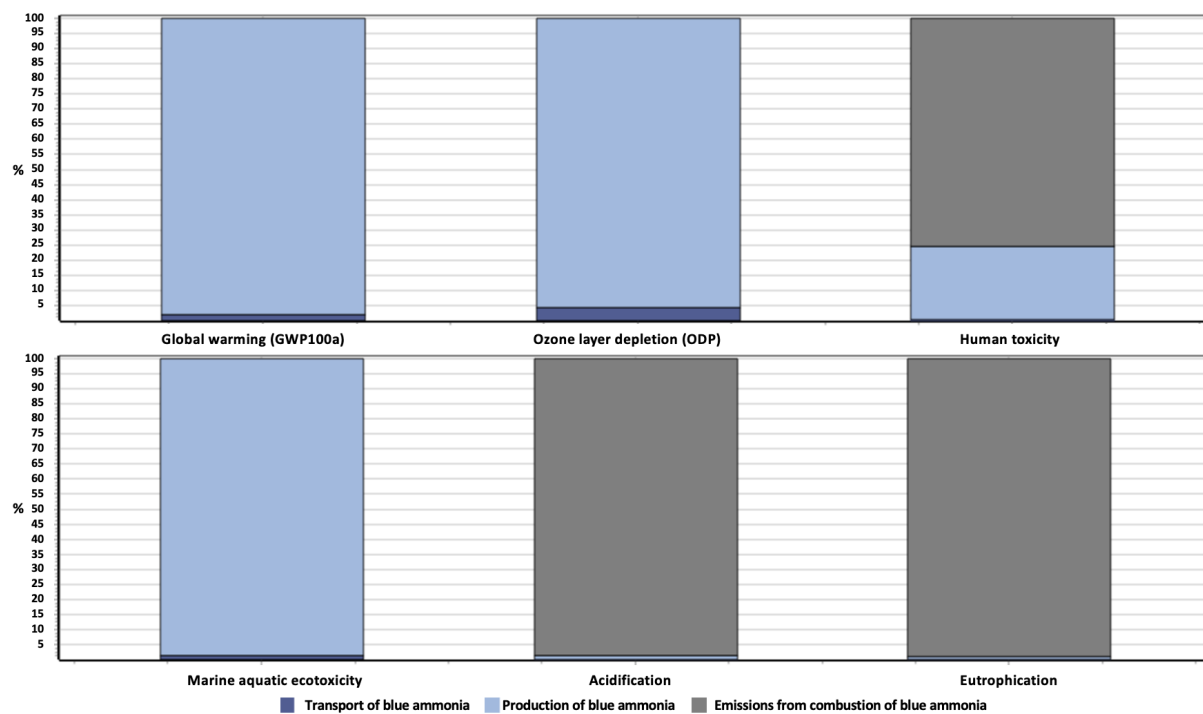
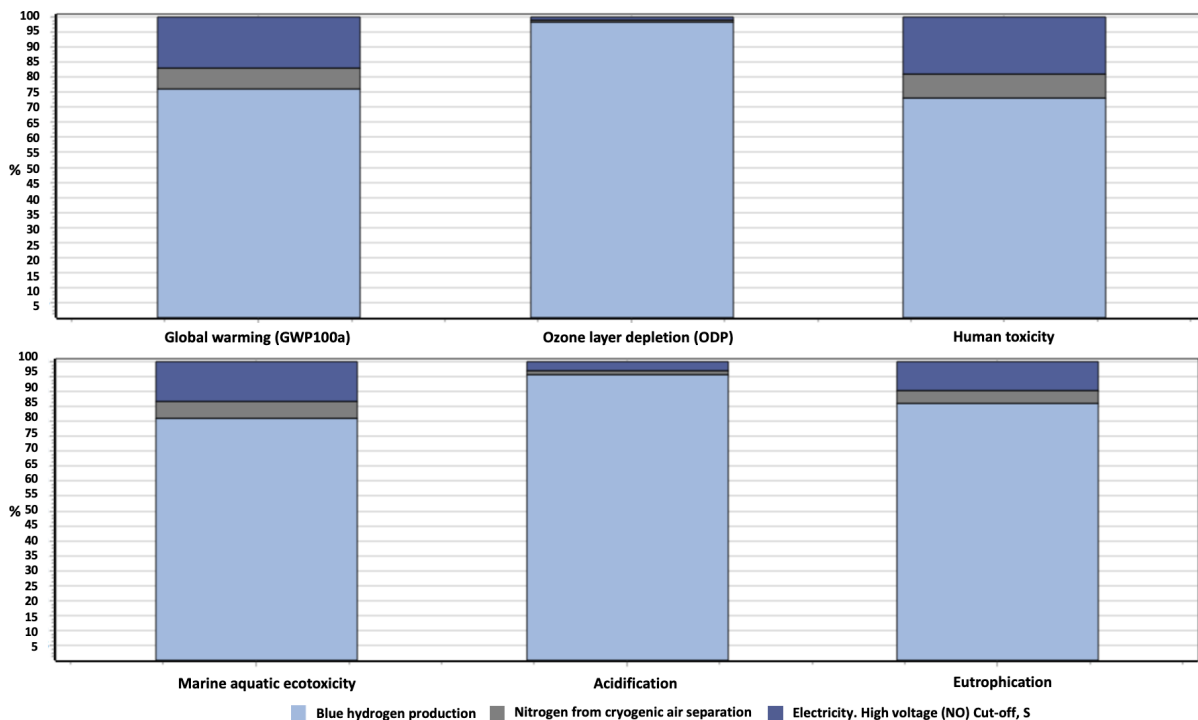


Figure 4.7: By taking a closer look on the LCA of ammonia, it is easier to locate which of the components through its life cycle contribute the most to emissions, out of production, transportation and utilization.

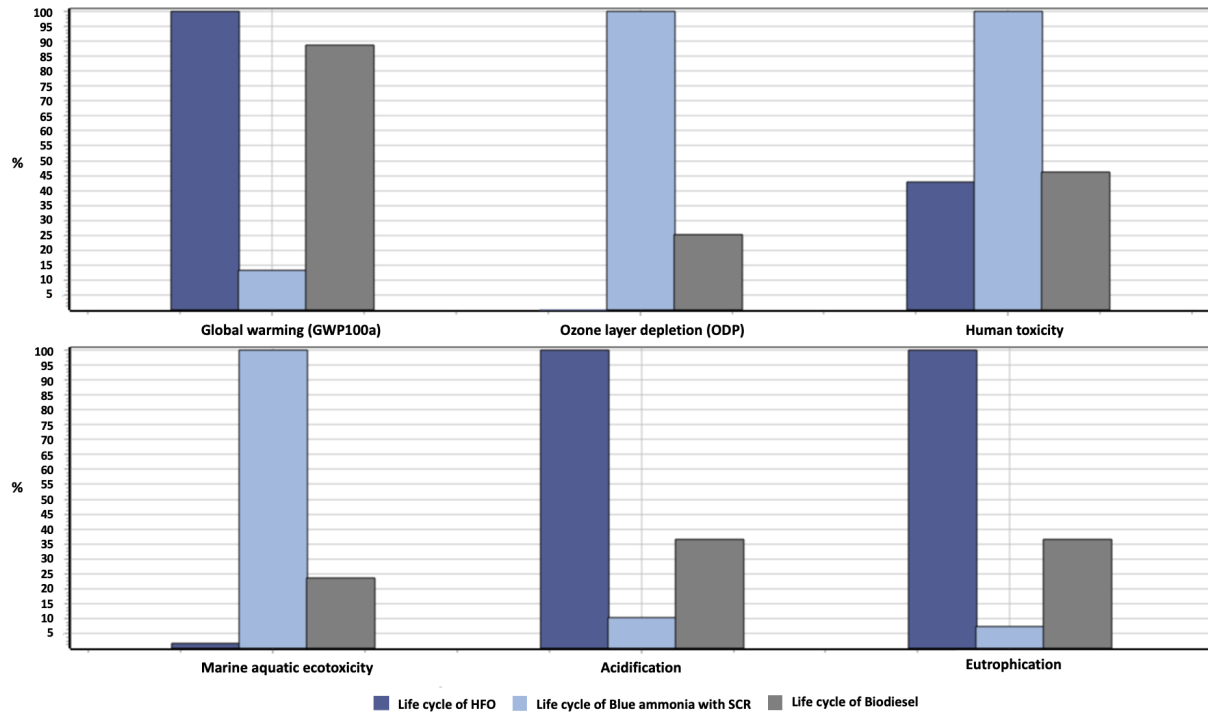
By zooming in even further on ammonia, a more comprehensive understanding of the impact of each component during the production process can be obtained. Figure 4.8 has been created to highlight the key elements of ammonia production that play the most significant role when it comes to emissions. Hydrogen has a noticeable larger effect on the impact categories compared to the other inputs. This aids in better understanding where the focus should be directed, and where emissions reduction is wanted.



Method: CML-IA baseline V3.07 / EU25 / Characterization / Excluding infrastructure processes
 Analyzing 217 ton "Production of Blue ammonia"

Figure 4.8: By zooming in even more on the production of ammonia, it can be established which of the inputs have the largest impact on emissions.

Figure 4.9 shows the scenario if SCR were to be implemented in the engine. This changes the outlook of ammonia compared to Figure 4.5 in several impact categories. It can be seen that there is a significant decrease in the overall emissions in categories such as acidification and eutrophication compared to the scenario without the implementation of SCR.



Method: CML-IA baseline V3.07 / EU25 / Characterization / Excluding infrastructure processes
 Comparing 1 p "Life cycle of HFO", 1 p "Life cycle of Blue ammonia – with SCR" and 1 p "Life cycle of Biodiesel"

Figure 4.9: By implementing SCR to remove NO_x emissions from combustion, the comparison of the fuels change significantly in several impact categories. Especially acidification and eutrophication, which are affected mostly by NO_x .

4.4 Economical considerations

An economic analysis was done to compare the feasibility of the new sustainable marine fuels, ammonia and biodiesel, to HFO. HFO are already well established in the marine fuel market, and is therefore ideal to use as a reference. The analysis considers costs tied to the whole life cycle of the fuels, even though these costs may be split amongst several industries. This economic analysis will consider the costs of emissions found in the LCA as well as cost of the required amount of fuel for this case. Affects of possible increases in CO₂ price are also looked into for an impression of future feasibility in the marine fuel market.

4.4.1 Economic choices and constraints

To be able to do an economic analysis of the the fuels throughout their life cycle, prices for different costs had to be found. This section will present and comment on the values that were found. Most values were found from different literature. All currencies were either found in USD or converted using exchange rates from 11.05.2023. This section will further describe the methods and equations used for the analysis.

Table 4.12 shows the price of the fuels compared in the case study, price of diesel for the trucks and the price for CO₂ and NO_x emissions. The price of fuels is based on the selling price. The data have been gathered from sources that are constantly changing, the price are thereby sat according to the price given on 11.05.2023. Potential costs from other emissions were neglected due to the lack of available data, and the quantities of these emissions were not substantial enough to make grounds for comparison.

Table 4.12: Cost of fuels and emissions in suitable unit.

	Price	Unit
Blue ammonia [79]	0.5	UDS/kg
Biodiesel [24]	1.49	USD/kg
HFO [131]	0.62	USD/kg
CO ₂ [136]	0.1	USD/kg
NO _x [5]	1.28	USD/kg
Diesel [116]	1.75	USD/L

Ammonia price

The price of ammonia from natural gas follows the gas market. There has been assumed that CCS adds to the ammonia price. The production cost of ammonia from natural gas ranges from USD110-340 per metric tons, and CCS would add about USD110-340 per metric tons to these costs. This would bring the price of production up to USD210-490 per metric tons [79].

Ammonia prices has been reported to range between less than USD200 and up to USD700 per metric tons over the past decade. The average ammonia price for 2008 to 2017 was about

USD400/t [79]. Considering this average price and the production price of blue ammonia, it has been assumed a ammonia price of USD500 per metric tons. This correlates to 0.5 USD/kg.

HFO price

The average HFO prices in several countries globally ranged from 400-700 USD/metric tons in 2020 [76]. Based on this it was assumed that the price would be around 600 USD/metric tons. The average price globally of HFO found on 11.05.2023 was 620 USD/metric tons [131]. This price was therefore chosen for the analysis because it was close to the assumed price and represented a global average.

Biodiesel price

The price of biodiesel depends on the amount of biofuel that are in the diesel. The price estimation for this case was done with B100 which is a pure biodiesel that contains 100% biofuel. An average of 5.22 USD/gallon, found in a report from the U.S. Department of energy, was chosen for the analysis. This can be converted to 1.49 USD/kg [24].

Diesel price

The average price for diesel in Norway between February and May 2023 was 1.88 USD/L. For comparison, the average price of diesel in the world for the same period was 1.73 USD/L. The diesel price on 11.05.2023 was 1.75 USD/L [116].

The average price of diesel in Norway between April 2020 to January 2023 was 17.55 kr/L. This is 1.61 USD/L [44]. Considering this and the more recent average prices it was chosen to use the diesel price found on 11.05.2023 which was 1.75 USD/L.

CO₂ price

Norway joined the EU Emissions Trading System (EU ETS) in 2008. This means that Norwegian industries that this system applies to need to follow these regulations for emissions [112]. The average price of CO₂ from 2005 to 2023 is about 94 EUR/metric tons [45]. This is about 100 USD/metric tons.

Norway also has their own carbon tax on releases of CO₂ and natural gas. The carbon tax for 2023 is NOK 2.03 (USD 0.19) per liter of oil or condensate [112]. This would not contribute in significant amount to the overall CO₂ price, and the price was therefore estimated to be 100 USD/metric tons from the average ETS CO₂ price. This can be converted to 0.1 USD/kg.

NO_x price

The NO_x tax is payable on emissions of NO_x coming from energy generation from some sources. The excise duty applies to emissions in Norway and on the Norwegian Continental Shelf. It covers

emissions from shipping in Norwegian territorial waters, although some parts of the shipping happens outside these territorial waters [5].

The price for NO_x emissions are currently priced NOK 24.46 which correlates to USD1.28 [5]. This was found on the Norwegian tax administration's websites.

Costs

Cost of trucks for transportation of ammonia is neglected because it is assumed that Yara, the ammonia producer, will provide their own. Transportation costs for HFO and biodiesel were also neglected because it is assumed that they are produced near the utilization site, and therefore will be minimal.

Equation 4.6 was used to find the costs for producing the required amount of each fuel. The amount of fuel required given in Table 4.3 was multiplied with the fuel price in USD/kg fuel found in Table 4.12, for each fuel.

$$C_{fuel} = P_{fuel} \cdot m_{fuel} \quad (4.6)$$

Equation 4.7 was used to find the costs for CO_2 emissions connected to the whole process of production, transportation and utilization for each fuel. The amount of CO_2 eq in kg that was found in the LCA in SimaPro was multiplied with the CO_2 price in USD/kg found in Table 4.12 for each fuel.

$$C_{\text{CO}_2 fuel} = m_{\text{CO}_2 fuel} \cdot P_{\text{CO}_2} \quad (4.7)$$

Equation 4.8 was used to find the costs for NO_x emissions connected to the combustion process for each fuel. The reason for only looking at emissions of NO_x from the utilization process was that this is where they are most evident. The amount of NO_x emissions found from Equation 4.5 was multiplied with the NO_x price in USD/kg fuel found in Table 4.12 for each fuel.

$$C_{\text{NO}_x fuel} = P_{\text{NO}_x} \cdot m_{\text{NO}_x fuel} \quad (4.8)$$

Equation 4.10 was utilized to calculate the transportation costs for ammonia. HFO and biodiesel was produced near the utilization site so the cost of transportation of these were therefore neglected. The amount of diesel required for the transportation of ammonia, found in Equation 4.4, was multiplied with the diesel price in USD/L found in Table 4.12.

$$C_{trans_{fuel}} = P_{diesel} \cdot m_{diesel} \quad (4.9)$$

Total costs was found by adding the costs for the fuel, CO₂ emissions, NO_x emissions and transport found from Equations 4.6, 4.7, 4.8 and 4.10 respectively.

$$TC_{fuel} = C_{CO_2_{fuel}} + C_{fuel} + C_{NO_x_{fuel}} + C_{trans_{fuel}} \quad (4.10)$$

The effects of an increase in the CO₂ price of 20%, 40% and 60% was found using Equation 4.11. SCR technology, described in Chapter 2.3.2, was used to reduce the NO_x emissions significantly. The NO_x taxation cost were therefore neglected for relevance and comparison purposes. The CO₂ price in USD/kg found in Table 4.12 was multiplied with the percentage change to find the new price. This new price was further multiplied with the amount of CO₂ eq in kg that was found in Chapter 4.3.3 to find the new cost of CO₂. The fuel cost and transportation cost were then added to the new CO₂ cost to find the new total cost.

$$FC_{fuel} = m_{CO_2_{fuel}} \cdot P_{CO_2} \cdot (1 + x_{\%increase}) + C_{fuel} + C_{trans_{fuel}} \quad (4.11)$$

4.4.2 Economic results

This section presents the results of the economic analysis based on the data collection and methods described in Section 4.4.1 above. The primary emphasis will be on the fuel costs and expenses associated with NO_x and CO₂ emissions resulting from the use of fuels. Matlab has been used as a tool to calculate and illustrate the different costs. This will give an insight of which costs impact the total costs of each fuel the most, as well as the effect of a 20%, 40% and 60% increase in CO₂ price. The calculations done for these results are shown in Appendix C.

Figure 4.10 shows the fuel and emission costs for the amount of each fuel required in the case. The costs for CO₂ emissions and for NO_x emissions for each fuel are indicated in Figure 4.10a and 4.10b respectively. HFO and biodiesel has significantly higher costs for CO₂ than ammonia. Cost of NO_x emissions are relatively higher for ammonia compared to biodiesel. HFO has about half of the cost for NO_x than ammonia. Figure 4.10c show the cost of the required amount of fuel for the case. HFO has the lowest fuel cost, and biodiesel has the highest fuel cost. Ammonia also has a significant fuel cost. The total costs including CO₂ emissions, NO_x emissions, transportation and fuel cost are indicated in Figure 4.10d. The cost contributing most to the total cost for HFO and biodiesel are the fuel cost. The total cost of ammonia is largely from the NO_x cost.

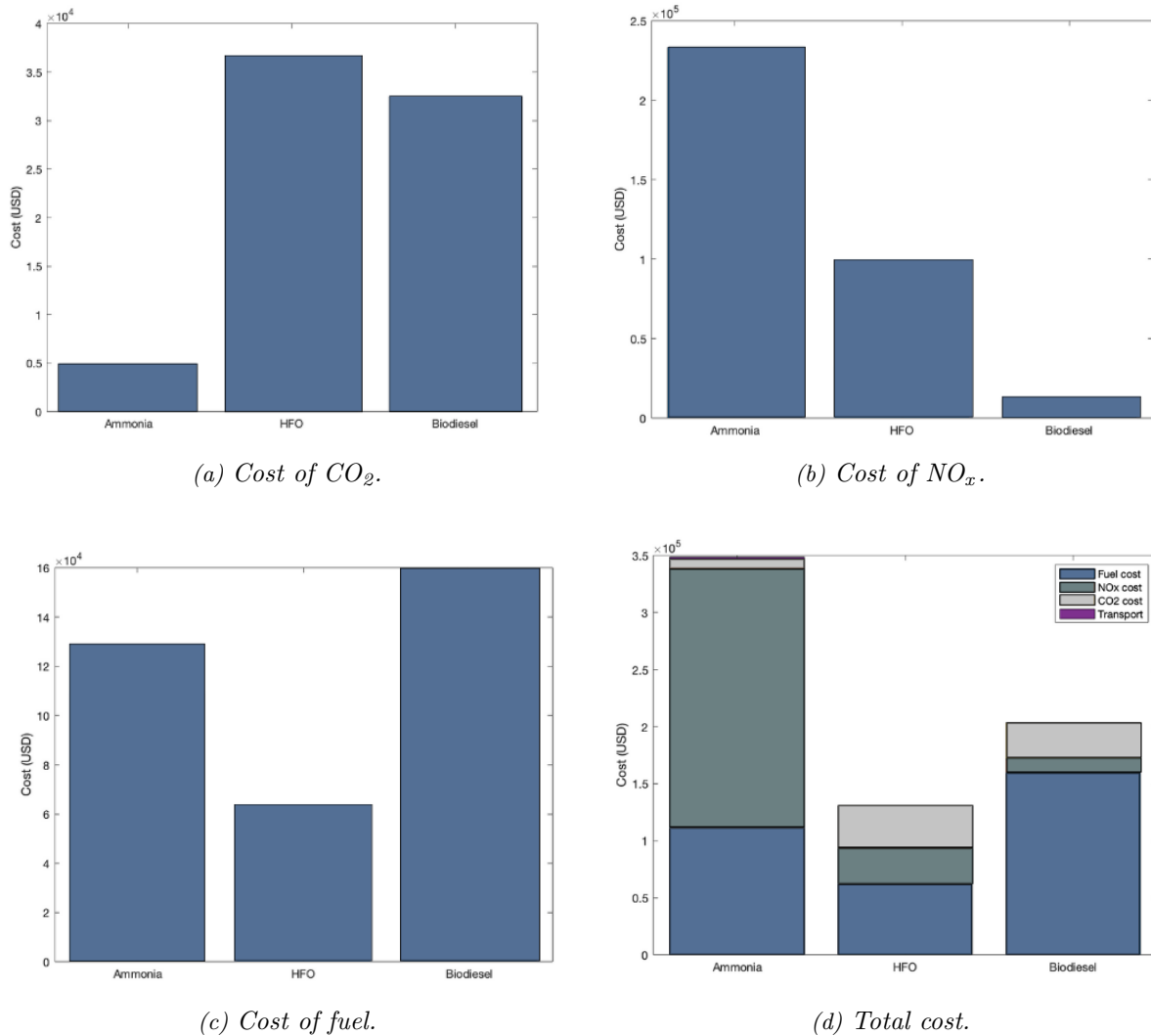


Figure 4.10: Fuel and emission costs for each fuel.

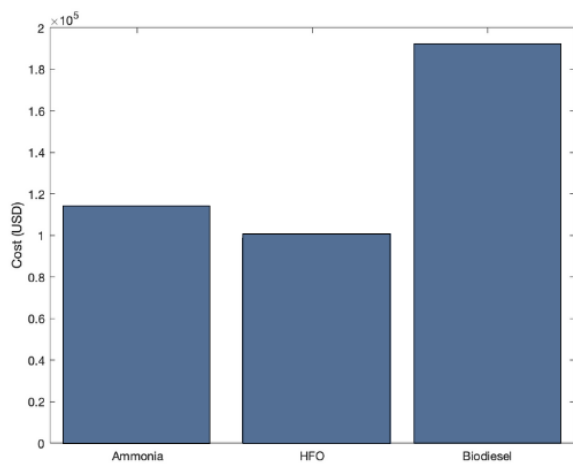
Table 4.13 shows the costs of the fuel, CO₂, NO_x and the total cost for each fuel.

Table 4.13: Costs of fuel, CO₂, NO_x and total costs for each fuel.

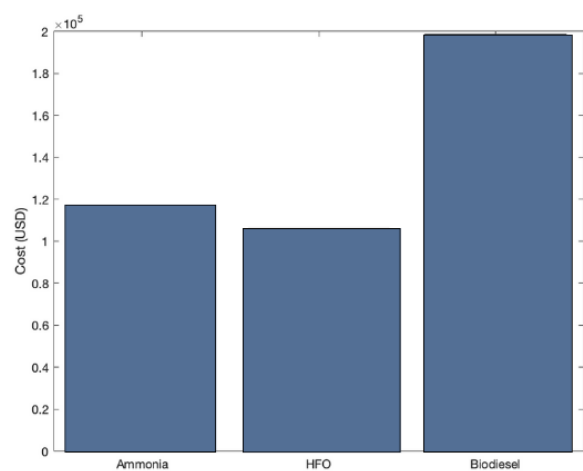
	Blue ammonia	HFO	Biodiesel
CO ₂ cost (USD)	1.06e+9	3.66e+9	3.48e+9
NO _x cost (USD)	2.33e+5	3.19e+4	1.17e+4
Transportation cost (USD)	1.47e+3	0	0
Fuel cost (USD)	1.09e+5	6.23e+4	1.60e+5
Total cost (USD)	1.06e+9	3.66e+9	3.48e+9

Figure 4.11 indicate the total cost for each fuel with different CO₂ prices with SCR technology. Today's total costs per kg fuel are indicated in Figure 4.11a. Figure 4.11b, 4.11c and 4.11d show the effects on total cost for increases in CO₂ price of 20%, 40% and 60% receptively. An increase of 20% reduces the difference in total cost for the fuels. An increase of 40% puts ammonia and HFO at approximately the same total cost. HFO has a higher total cost than ammonia when the CO₂ price was increased with 60%. Biodiesel has a higher total cost compared to HFO and

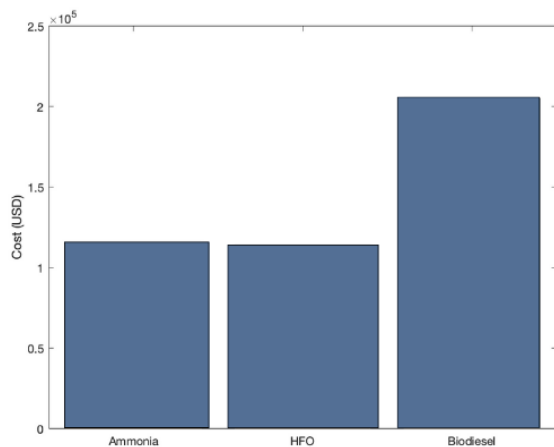
ammonia for all CO₂ price increases.



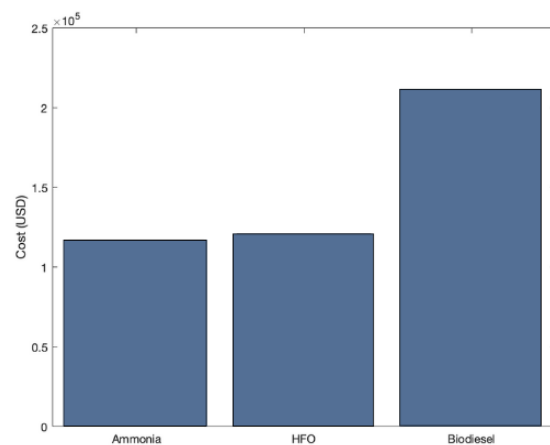
(a) Today's CO₂ price.



(b) 20% CO₂ price increase.



(c) 40% CO₂ price increase.



(d) 60% CO₂ price increase.

Figure 4.11: Total cost with SCR and different CO₂ prices for each fuel.

Table 4.14 shows the total cost for each fuel with SCR using the original CO₂ price, and with increases of 20%, 40% and 60%, respectively.

Table 4.14: Total cost for each fuel with original CO₂ price, and with increases of 20%, 40% and 60%.

	Blue ammonia	HFO	Biodiesel
Total cost (original CO ₂ price) (USD)	1.15e+5	9.89e+4	1.92e+5
Total cost (20% increase) (USD)	1.16e+5	1.06e+5	1.98e+5
Total cost (40% increase) (USD)	1.17e+5	1.14e+5	2.05e+5
Total cost (60% increase) (USD)	1.18e+5	1.21e+5	2.12e+5

5 Discussion

Ammonia as a fuel

The ammonia currently produced is primarily classified as gray and accounts for 1% of total GHG emissions annually. Changing the production methods could contribute to a large cut in these emissions. Yara is the primary producer of ammonia in Norway, and their current production is exclusively focused on gray ammonia. Their priority for future production is to introduce CCS to their production facilities. Natural gas steam reforming with CCS could therefore be seen as a greener production method closer in the future than renewable production. The CCS technology are new to the market and are high-priced. The CO₂ prices need to be high enough for the investment in CCS technology to be beneficial.

The production of ammonia happens in three parts; hydrogen generation, nitrogen generation from air separation and the Haber-Bosch process. The Haber-Bosch method is the main ammonia synthesis method, other technologies for ammonia production has the potential to be researched further. The reduction in emissions could largely be done in the hydrogen production process.

Production methods for hydrogen such as electrolysis are a good substitute to fossil based production. It has zero carbon emissions and operate at low temperatures. The problem with this production method is the energy sources used for electricity supply. The Hydrogen production will be green when connected to energy sources that are renewable, but these sources are not always available or the most cost-effective option. Hydrogen generation from electrolysis also has high capital costs and requires high pressure.

Methane pyrolysis is believed to be a GHG neutral process, and thermochemical water splitting has the potential to have zero GHG emissions, as described in Chapter 3.1.1. These technologies are potentially good hydrogen production substitutes to fossil production, but they are not commonly utilized in large-scale hydrogen production today. Methane pyrolysis does not emit CO₂, but it still has a carbon byproduct and the production is dependent on fossil fuels. Thermochemical water splitting has a dependent feedstock but it is not yet commercialized and has high capital costs.

Gasification using coal or biomass is another hydrogen production method to consider. Gasification of coal has been commercialized, but it requires high temperatures and results in substantial carbon emissions. Biomass is another feedstock used for gasification that are considered green. The problem with biomass is that the hydrogen yield depends upon the feedstock which might be seasonal. Another concern is the potential competition for resources with other sectors such as food production.

Natural gas steam reforming are one of the most common and cost effective methods for hydrogen production. This method are standardized for large-scale production today, and was also chosen for the case study in combination with CCS. This method has the most developed technology and existing infrastructure. CO₂ are a byproduct from this method, but this can be reduced with 90% when introducing CCS technology. While relying on natural gas has negative environmental implications, it remains a stable and comparatively affordable feedstock.

Cryogenic distillation are commonly used in large-scale nitrogen production today because of its low energy consumption and high purity. This production method has a high capital cost and limitations when it comes to capacity. Membrane nitrogen generation, an alternative air separation method, has both low capital cost and are more flexible in the product output when it comes to both quality and amount. Membrane air separation are only used in small-scale nitrogen production because of its low purity and high energy consumption which could make it more expensive and contribute to more GHG emissions. The low purity is also a drawback when the nitrogen is going to be used in ammonia production. Pressure swing adsorption produce high purity nitrogen at an affordable cost, and could therefore be viewed as a good alternative to cryogenic distillation. The reason why it is not considered a better alternative might be because of the problems concerning maintenance and the noise pollution.

Ammonia has been stored and handled for many years by the fertilizer industry. There are well established routines and requirements for storage and handling of ammonia because of this. Routines and regulations regarding ammonia used as a fuel could therefore easily be put in place to get it certified by IMO. The same technologies and methods used by the fertilizer industry for transportation and storage could to some degree be used in the maritime sector. This is a advantage compared to other newly introduced renewable fuels, and could possibly lower the barrier for commercializing ammonia as a maritime fuel.

Ammonia could possibly be used as a hydrogen carrier. Ammonia liquefies at -33°C or at the pressure 8.6 bar, while hydrogen require a temperature of -253°C to liquefy. This is one of the main reasons to why ammonia could be used as a hydrogen carrier. Liquefying hydrogen requires cooling work that is equivalent to around 20%-30% of the energy that the hydrogen holds. There is less energy needed to liquefy ammonia and it is not as flammable as hydrogen. The drawbacks to ammonia as a hydrogen carrier is its toxicity and the additional costs of cracking. There are also some potential energy losses when converting the ammonia back to hydrogen. All these factors need to be accessed against each other when considering ammonia as hydrogen storage.

Two- and four-stroke engines

Utilizing ammonia directly as a fuel, partly decomposed, or blended with other fuels, can have many significant advantages.

IC-engines is capable of using ammonia directly and have been researched in many decades. The primary advantage of burning ammonia directly in the engine is that it reduces the threshold for transitioning to a greener fuel. This is because there is no need to replace the ship or undergo expensive modifications, making the transition more cost-effective and feasible.

One issue is the high auto-ignition temperature ammonia requires. Because of this, it is necessary to use glow plugs or pilot fuels. Hydrogen and diesel used as pilot fuels alongside ammonia leads to increased emissions, contrasting the emissions reduction potential of using ammonia alone. It is possible to have different ratios of ammonia and hydrogen. This aspect has been investigated using a four-stroke engine, revealing that it enhances ignition performance. It is possible to implement cracking to only crack a portion of ammonia to make a ammonia-hydrogen blend, but this acquires more space on the vessel.

Upon examining the conventional engines commonly utilized in the maritime transport sector, it becomes evident, as discussed in the Chapter 2.3, that both two-stroke and four-stroke IC-engines exhibit suitable characteristics for long-distance shipping.

Comparison of four and two stroke engines

The four-stroke and two-stroke are both broadly used in the maritime market but the two-stroke engine is more commonly installed. The four-stroke engine, although having a compact plant size and a higher revolution rate, is outclassed by the two-stroke engine in various factors.

Two-stroke are the preferred engine system for large vessels. Having twice as many power strokes per crank revolution compared to the four-stroke engine, it is more efficient as it reduces both mechanical and thermal losses. Having said that, the power output per unit displaced volume is less than twice the power output of an four-stroke engine at the same speed.

Due to the fact that the two-stroke engine is lighter in weight than the four-stroke engine, it results in a higher power-to-weight ratio. The two-stroke engine is considered more cost-effective due to its smaller size, lighter weight, and simpler construction in comparison to the four-stroke engine. Consequently, vessels equipped with two-stroke engines can transport more cargo while maintaining the same power output. As the size of the engine increases, so does its weight and the amount of space it occupies. In the shipping industry, both space and weight are crucial factors to consider. This is because, in addition to fuel consumption, a ship's capacity to carry more cargo while maintaining the same power output is directly influenced by the available space and weight constraints.

Fuel cells

Regarding fuel cell technology, there is multiple fuel cells that has potential to produce electricity to power an IC-engine with the help of ammonia. SOFCs can use ammonia directly and has the potential to have a higher efficiency than two-stroke engines. The PEMFC is a fuel cell that is

already in use in electric vehicles and has some benefits that it is getting more cost-effective and it is small in size. Ammonia can be used to power PEMFC indirectly by splitting the ammonia into nitrogen and hydrogen with the help of cracking on the boat. The same goes for MCFCs. This fuel cell is available in the market as well but has a short life time and have high costs.

Cracking towards hydrogen and nitrogen happens over a catalyst in a cracking reactor as described in Chapter 3.1.4. The temperature required for the reaction depends on the catalyst chosen. PEMFCs for instance, has a relatively low operating temperature of 60-100°C, compared to other fuel cells. Cracking on the boat could be difficult as many of the catalysts has a required temperature well above this operating temperature. Another issue with the high temperature is the maintenance of it. Hydrogen or ammonia need to be combusted, to be able to maintain the high temperatures needed onboard a boat if there is no access to other energy sources.

Many fuel cells also need a high purity of hydrogen to operate. PEM cells need less than 0.1 PPM concentration of ammonia to be present. There could therefore potentially be necessary with a purification process that removes the unconverted ammonia. This could add additional costs and the benefits of using ammonia as hydrogen storage need to be weighed up against the drawbacks.

The cracking process could potentially be done on shore and not on the ship. This would avoid the problem with high temperatures required in the cracking reactor being in conflict with the relatively low operating temperatures for some fuel cells. There would also be access to other energy sources to avoid the combustion of ammonia or hydrogen to maintain the temperature. On the contrary, the advantages of using ammonia as a hydrogen carrier would be eliminated by moving the cracking process on shore. The hydrogen would then need to be stored on the ship, which is a much more complicated process than for ammonia.

PEMFCs generally have lower output power, making them better suited for smaller vessels. For longer distances like the one traveled by the Fure Valö, higher power requirements are necessary. MCFC and SOFC are considered more fitting for longer distances like Mongstad to Reykjavik, but to deliver sufficient power it requires a large and heavy fuel cell stack which again comes at the expense of the weight of the boat. Current fuel cell systems are still remarkably more expensive than traditional generators, and the technology is not ready to be used. With time it is anticipated that the cost will reduce when the technology becomes more mature and the high investment cost is justified by the advantages.

Because of cost, robustness, available technology and power density, IC-engines are regarded to be a better option than fuel cells in the years to come.

Engine choice

Even though the two-stroke engine is a good choice, the ship Fure Valö used in the case operate

with the Wärtsilä dual-fuel four-stroke engine. In Chapter 3.6.1 it was mentioned the dual-fuel two-stroke engine from MAN Energy solutions. This engine is not commercialized and therefore not available yet. The Wärtsilä engine was chosen based on the current research happening on Fure Valö with this exact dual-fuel engine. This engine can not only work with HFO, LNG, and biofuel, but is capable to utilize ammonia in the near future. The safety and handling technology are already in use because it can operate on LNG, but since the route is in emission control areas, it can operate on low-emission fuel and switch between fuels without losing power. This makes the transition from conventional fuels to ammonia or other clean fuels more seamless.

There are some potential improvements for IC-engines to reduce emissions like NO_x and SO_x . As mentioned in Chapter 2.3.2 can scrubbing be a solution to remove SO_x by more than 80%. Some advantages with scrubbers is that it can be implemented on already existing ships and can help ships meet the emission regulations like IMO standards. There are some disadvantages to scrubbers as well. It can be expensive to install and it does not reduce any other emissions than SO_x . It can also increase water pollution if the wash-water is not properly treated and discharged.

SCR can remove NO_x up to 95%. Like scrubbers they help ships meet the emission regulations, and helps to reduce the tax that comes with the emissions of NO_x . They can be retrofitted to existing ships, but they can also be expensive and do not reduce any other emissions except NO_x .

CO_2 can be captured before it is emitted to the air by capturing it from the main engine before it passes through the exhaust outlet. Since it reduces emissions from ships, it can make HFO more sustainable than it is today. CCS is still researched and developed and it is expensive. It also needs a suitable place to store the CO_2 like for example the seabed as mentioned in Chapter 3.3. This is extremely expensive as it requires pipelines to transport the CO_2 under the seabed.

It is also mentioned that MCFCs can run on the exhaust gas from a power plant. This fuel cell is the only post-combustion CCS-system that generates a energy production. If the technology allows for it, it could be possible to implement MCFCs on ships to work with IC-engines so it could produce electricity to other areas on the boat and at the same time capture carbon.

Alternative fuels

When considering the various fuels currently in use and those being considered for the future, it is important to weigh the numerous benefits and drawbacks against one another. One thing is for sure, it is necessary to cut the emissions, and find more sustainable ways to travel the worlds oceans. There might be more than one solution to this problem, it is therefore important to consider all available options.

HFO has been widely utilized in the maritime sector primarily due to its widespread availability

and affordable price. It does however have high emissions, and relies on fossil fuels, making it an unsustainable choice for the future. There are available options to minimize the emissions from HFO during combustion. Processes that removes SO_x and NO_x can be implemented, as well as CCS technology on-board. This has the ability to reduce the emissions significantly, this will however affect the overall price of HFO.

HFO and the other fossil-based fuels such as MGO and LNG can be affected by limitations regarding availability in the future. It is therefor a reason for looking into alternative fuels that are not based on fossil sources, to ensure that it will be possible to meet the energy and fuel demand in the future. Even though there are technologies that can reduce the emissions during combustion, this might only be a short term solution. This should open the door for transitioning into renewable sources. Emissions is one thing, but availability will also play a significant role in the future.

Methanol is another alternative fuel that has been considered more in the maritime sector. It offers safety benefits due to its low flammability, making it a favorable choice in terms of safety considerations. In addition, it has low production costs. It holds some of the same disadvantage as HFO, LNG and MGO as it is difficult to find ways to produce it from renewable energy sources. It also require a larger volume on-board. Since it holds a lot of similar advantages and drawbacks as HFO, it is unnecessary to do further research on this specific fuel. It would likely show a lot of similar results as HFO.

There are several new alternatives that are considered along side ammonia. Hydrogen has a broad flexibility in production. A reason for not doing further research on hydrogen as a fuel is based on its difficulty to handle and store since it is utilized in the form of gas. Hydrogen is also used to produce ammonia, there will therefore be a lot of similar emissions tied to production. It can also be seen in Figure 4.8 that hydrogen is the main source to emissions when producing ammonia. It was seen as unnecessary to compare ammonia and hydrogen as fuels seeing that they have similar components. The benefit hydrogen holds over ammonia is that it offers a much higher energy density, which essentially means that less fuel is required. Hence, having less emissions from production and combustion. Hydrogen does however have several disadvantages tied to safety.

Electrical power is another alternative fuel that could be compared with ammonia. The main disadvantage associated with batteries is that it needs to be charged. In order to cover longer distances without the need for frequent stops, larger-sized batteries are required. However, this poses a challenge as it consumes a substantial amount of onboard space. For cargo ships, this might work against its purpose. It would also require resources for manufacturing charging stations. Another disadvantage mentioned in Section 2.1 is that the recharging of the batteries

is more time consuming than refueling. Electrification of the marine sector should certainly continue, it is however not suitable for all distances at this time. It might gain more flexibility in combination with fuel cells. So far, it might be best suited for short distances, with the opportunity for charging at each stop, to ensure energy delivery. For the chosen route and purpose, electrical power stored in batteries was not considered a suitable option to be compared with ammonia. They do not have the same ground for comparison, it was therefore considered to not be optimal, since the battery require a lot more adjustments on the vessel, as well as the infrastructure on shore.

Numerous benefits have been identified in the use of biofuels, particularly biodiesel. The ideal blend would be 100% biodiesel, B100. It offers significant flexibility in terms of the sources used for its production. There is also a wide range of flexibility in determining the desired percentage of biodiesel in a blend, depending on performance and availability. The issue with choosing a B100 blend is that there is not enough research on performance. It is therefore unknown how well this fuel can perform. The choice of biodiesel was based on a project done by "Fure Valö" where they tested a B30 blend, showing good performance results. It has therefore been assumed that it is possible for B100 to complete the same distance without too many complications.

Results from case

Choosing to compare biodiesel and HFO with ammonia was based on having a reference point. Thereby using the most commonly used fuel, and another future fuel that holds different components. The three fuels give a variety of the different alternatives, and a good starting point for comparison. This approach offers the most accurate representation of the current situation. It is clear that new alternatives should be considered. The reason for not comparing the possible scenario for HFO is that the base for comparison is supposed to show a reason for new thinking. The focus is not on making improvements for HFO, although it is indeed a possibility that should be taken into consideration.

The limitation of the system boundary is considered to cover enough steps of each life cycle, to give a common ground for comparison. The assessment takes into account the emissions and costs associated with production, transportation, and utilization. The manufacturing processes of refineries, production plants, and the materials used for production are deemed irrelevant in this context. The goal was to complete a good enough comparison of the fuels, to further know what can give the best economical and sustainable benefits in the future. To give the fuels a good base for comparison it was decided to convert the functional unit emissions and cost to per kg of each fuel, and thereby relate this to the required amount to cover the distance.

The inventory lists are predominantly based on available data and tailored to meet the requirements of the system boundary. Based on it being a comparative LCA, it can still

be considered a cradle-to-grave analysis. The reason for this is that parts that involve similar processes and equipment is neglected, because an increase for one, will be the same for all. The ship and engine used for transportation is the same for all, and is also a reason for choosing the specific engine, since it can be used by all three fuels. This goes hand in hand with deciding on the three fuels to begin with.

The calculations conducted in the case demonstrate that the specific route necessitates more than double the amount of ammonia to complete the transportation. The supply energy derived from ammonia is less than half than what it is for HFO. This leads to ammonia taking up more space during transportation, and will also require more space when used as fuel. This essentially means that if the tanks were filled up to maximum capacity, ammonia would take the vessel half the distance as HFO and biodiesel. This makes ammonia the less efficient fuel out of the three. This was one of the three major points for comparing the fuels. The case study clearly show that ammonia is less efficient. It does not affect this specific route, since the tank has the capacity for all three, but it could certainly be a case for longer distances.

The reason for choosing the specific impact categories in Table 4.10 is that they are suitable when comparing the fuels. It covers the part of each life cycle that mainly is considered, which is production and utilization of the fuels. Considering global warming potential is crucial as it aids in assessing the overall environmental impact within the given sector. This finding can contribute to informed decision-making regarding the choice of fuel to be utilized in the future. It is also important to take human health into account when comparing the fuels. Human toxicity is therefore another important impact category, since it evaluate exposure to toxic substances. The potential risk workers, and the community around, are exposed to toxic substances when producing and utilizing the fuels and should be carefully considered. The ozone layer is highly important to consider as it serves a vital role in protecting the Earth from harmful UV radiation emitted by the sun. Acidification and eutrophication is primarily chosen because of the NO_x emissions when ammonia is combusted. The impact of this should also be evaluated, to further know the risk of acid rain caused by unbalance in the nitrogen cycle, which ammonia has a risk to contribute with.

Due to ammonia's zero-carbon combustion properties, its CO_2 emissions are exclusively associated with the production phase. The bar chart in Figure 4.5 show that ammonia performs remarkably better than the two other fuels when it comes to global warming potential, meaning that it has the least amount of CO_2 emissions in total. It does however not score well within the impact categories; ozone layer depletion, human toxicity, marine aquatic ecotoxicity, acidification and eutrophication. This assertion confirms that ammonia is indeed toxic. This is one of the main concerns associated with using ammonia, as it is related to its high NO_x emissions during combustion. This explains why certain impact categories were chosen, as they effectively

illustrate the environmental impact of ammonia.

The bar chart in Figure 4.7 confirm that combustion contribute to most of the emissions when it comes to human toxicity, acidification and eutrophication. These are three out of five impact categories where ammonia has the most unfavorable results out of the three fuels. One possible solution to reduce the overall impact of ammonia in these three categories is by implementing SCR. This technology can remove up to 95% of the NO_x emissions and can have a significant and vital impact on the overall environmental footprint. This improvement is illustrated in Figure 4.9. Ammonia has a turnaround from least sustainable, to most in the three impact categories by removing the emissions of combustion.

The factor that contributes the least to emissions is the transportation of ammonia from Porsgrunn to Mongstad. This part of the LCA differentiate ammonia from the two other fuels. HFO and biodiesel do not require any transportation as they are produced at the delivery site. It would be natural to expect this to affect the total emissions of the life cycle to a greater degree than the bar chart in Figure 4.7 displays. The ammonia is transported a total of 6,992 km, and require 8 trucks. However, it does not appear to significantly affect the overall emissions. The reason for this could be that the diesel consumption per km is less significant compared to the emissions from combustion and production, it is at least what can be interpreted from the bar chart. Although transportation is not a big contributor through the life cycle, it still counts as a factor overall.

Another crucial factor that impacts the life cycle of ammonia is its production process. It can be seen in Figure 4.7 that the impact categories most influenced by the production is global warming potential, ozone layer depletion and marine aquatic ecotoxicity. The two latter is the remaining impact categories where ammonia has the worst score out of the three fuels. It can, for this reason, be resourceful to take a closer look at the production of ammonia, to figure out which components have the highest effect.

By looking at the bar chart in Figure 4.8 is it possible to gain an insight of which elements have the greatest affect during the production of ammonia. By observing the chart it is evident that blue hydrogen is the most contributing factor to cause emissions. Even though it is blue hydrogen, it is still produced from fossil fuels. The CCS can only remove CO_2 , meaning that other GHG emission remain. This means that emissions such as NO_x , chlorofluorocarbons and methane can affect the ozone layer and marine aquatic ecotoxicity. The source of the emissions related to the production of ammonia is predominately tied to the hydrogen production. The focus should possibly be directed more to the production method of hydrogen, to reduce emissions.

There are several different ways to go about producing hydrogen. Natural gas steam reforming

was chosen because it is one of the most common ways to produce hydrogen to date, it is also the most competitive cost wise. Other alternatives should definitely be considered to make hydrogen and thereby make ammonia a more attractive fuel to produce. This has been discussed more in detail earlier in this section.

The key findings from evaluating the bar charts and tables related to the emissions throughout the life cycle of each fuel indicate that ammonia is perceived as the least sustainable option. It is important to note that emissions from combustion could improve significantly if SCR was to be included. The measure of CCS when producing hydrogen, does not seem to be enough. Changing to another production method might be necessary if ammonia are to be implemented as a future and lasting fuel.

Economy results

The economic aspect of the case considers costs of the fuels and emissions. The prices given in Table 4.12 used for the case, are estimations done with available data, and are a subject to change. This could possibly affect the results and it would be beneficial to do further assessments.

The bar charts in Figure 4.10 shows the fuel and transportation cost, and the external costs of emissions for each of the fuels in the case. Figure 4.10a shows that the cost of CO₂ are significantly higher for HFO and biodiesel. This is expected as the production process and combustion of these fuels have higher CO₂ emissions than blue ammonia. Ammonia emits NO_x when it is combusted, which causes additional taxation costs as Figure 4.10b indicate. The NO_x tax affects ammonia to a larger degree than the CO₂ costs affects HFO and Biodiesel. This could be because NO_x are more toxic to humans and therefore has a higher taxation than CO₂. The price for blue ammonia are close to the price of HFO, but the amount of ammonia required are doubled the amount of HFO which can be seen in the fuel costs in Figure 4.10c. Biodiesel is expensive and is therefore just above the cost of fuel for blue ammonia. Figure 4.10d shows that the total cost for ammonia are significantly higher than for the other fuels because of the high taxation on NO_x and larger amounts of fuel required. This could make blue ammonia difficult to implement in the maritime fuel market.

Figure 4.11 indicate the total cost for each fuel with different CO₂ prices. The percentage change in CO₂ price could have been chosen to be higher to further investigate the affects. Figure 4.11a indicate that the total cost for biodiesel are higher than for ammonia. HFO has a slightly lower total cost than ammonia. This is because the NO_x costs are removed, which contributed significantly to the total cost of ammonia. It is apparent from Figure 4.11b, 4.11c and 4.11d where the prices increase with 20%, 40% and 60% receptivity, that an increase of 40% are needed for ammonia to have approximately the same costs as HFO. The total cost for HFO are higher than for ammonia at a CO₂ price increase of 60%. Biodiesel have higher total cost in all four

bar charts, but the biodiesel total cost slightly approaches the HFO total cost as the CO₂ price escalate. This is because of the high price of biodiesel.

The key findings from evaluating the bar charts and tables related to the economic aspect of the case indicate that ammonia is the more expensive fuel option because of the high NO_x emissions and amount required. An increase in CO₂ price between 40% and 60% would be necessary to level out the total cost of ammonia compared to HFO.

5.1 Accelerating ammonia into the market

One might question why the production of blue ammonia was chosen for examination. Without doing any closer research on the production of green ammonia, it can be assumed that this is the most sustainable option. The main reason for starting with blue ammonia, is that it can be seen as a gateway into the market for ammonia. It primarily revolves around creating value for ammonia as a fuel. Before this can be done, it is important to consider the potential consequences. An evaluation of ammonia should be conducted to determine its suitability for future utilization. Green ammonia is currently considered to be prohibitively expensive. As a result, a more cost-effective option for producing the same product was chosen.

The case study reveals unfavorable results for ammonia, as its life cycle emissions are the highest among the three fuels examined. There is however a large degree of flexibility tied to the production of ammonia, which mainly relates to the variety in hydrogen production. The advantage that provides value for ammonia is its potential to be produced from renewable sources, unlike many of the marine fuels currently utilized, such as HFO, MGO, and LNG. The same applies to methanol, another alternative fuel under consideration, as it poses challenges in terms of green production. By adopting a futuristic perspective, there should be a strong emphasis on investing in renewable sources.

There are also several disadvantages with introducing ammonia into the market. Ammonia is known to be toxic, especially to marine life because of its NO_x emissions. This can be a hazard when considered ammonia as a fuel in the maritime sector. There are safety regulations already in place to minimize the risk. It is important to know which materials are used to store the fuel, to avoid corrosion. An advantage with ammonia is that it has a distinct smell, if there is a leakage it will be easier to detect, compared to other fuels such as LNG. This can contribute to preventing the situation from escalating further. Another upside is that the infrastructure required to handle fuels such as ammonia is already in place, so it would not require a great upheaval. The safety regarding leakages should for certain be accounted for when considering a possible market for ammonia. The toxicity of ammonia remains regardless of its production method, indicating that even green ammonia does not eliminate this concern. It has already been mentioned, but it is important to point out that there are technologies available, such as

SCR, that can help mitigate the impact of emissions, as previously discussed.

The issue does not only relate to the handling of the fuel on-board. The emissions from production is just as toxic as the situation currently is. Technologies like CCS can be implemented to reduce the CO₂ emissions. CCS is not a straightforward solution either, as it entails high costs compared to the economic benefits it offers for plants and refineries. It also require space for storage. Even if CCS is implemented when the production is based on fossil sources, there are still an noticeable amount of other GHG emissions, which are more difficult to capture. If the chosen production method in the case study were to be adopted as the standard for ammonia production in the future, it would not be considered environmentally beneficial.

Another downside associated with ammonia as a fuel is its low supply energy, which means that a larger volume is required compared to other fuels. The density of ammonia is also lower than most alternative fuels, which contributes to the increased volume demand. This translate into ammonia being a less efficient fuel than for instance HFO and biodiesel. The low supply energy not only affects the emissions through production and combustion but also has economic implications. Due to its lower energy content, a larger quantity of ammonia is needed to cover the same distance as the other fuels. Moreover, the volume requirements for ammonia can pose space constraints on vessels, particularly when they are used for transportation.

The production of fossil ammonia through natural gas steam reforming is dependent on the natural gas market. As gas prices rise, the cost of ammonia also increases. This was evident in 2021 when there was a significant increase in gas prices. The ammonia price then exceeded USD1,000 due to natural gas shortages. On the other hand, producing ammonia with renewable sources could decouple ammonia from the natural gas market. This could result in greener production, reduced reliance on fossil feedstocks and more predictable pricing. Consequently, it could make ammonia a more stable fuel option for the maritime sector. However, transitioning to a green ammonia production has its downsides. The cost of producing ammonia with renewable sources are generally higher, and the power supply for production may not necessarily come from renewable sources.

Currently, the price of CO₂ is set at approximately 100 USD per metric tons of emitted CO₂. However, according to the case study, for blue ammonia to become competitive with fuels like HFO, the CO₂ price needs to be increased by around 40%-60% compared to today's price. Such an increase in the CO₂ price would have a significant impact on fuels with high carbon emissions and could possibly lower the barrier for renewable fuels like ammonia to enter the fuel market. It would encourage a shift towards greener production and utilization of maritime fuels.

5.2 Recommendations for further work

Several factors associated with ammonia need to be thoroughly evaluated before knowing for certain if ammonia is an advisable fuel for the future. The case study in this thesis is based on blue ammonia from natural gas, which is an alternative that is not considered to be ideal. However it is important to recognize that there is potential for implementing improvements that can significantly reduce the environmental impact, thus making ammonia a more sustainable fuel option.

To gain a better understanding, further research on green ammonia is necessary, as it holds potential to be a prominent fuel in the future. If a substantial market for ammonia were to be created, it could lead to a reduction in production costs for green ammonia. It may then become competitive with fuels such as HFO and biodiesel in terms of ozone layer depletion and marine aquatic ecotoxicity. Additionally, implementing SCR during combustion would also remove an important amount of NO_x emissions. This would be beneficial looking at acidification and eutrophication, since these factors are strongly influenced by NO_x .

There are two possible solutions if this scenario is desired to be realized. One option is to invest heavily in green ammonia from the beginning, but it should be noted that there are no expectations of immediate profitability in the market. The other solution is to rely on the possibility that starting with blue ammonia would facilitate the future cost reduction of green ammonia. Regardless of the chosen path, change in the maritime sector is necessary to ensure future fuel delivery and achieve the decarbonization goals by 2050. Renewable sources should definitely be given more consideration and investment as we strive for a greener future.

Increasing the pricing of CO_2 emissions can contribute to a greater focus on sustainable production and utilization of marine fuels with lower emissions. When the cost of emitting CO_2 is higher, it becomes economically favorable for industries, including the maritime sector, to explore and invest in technologies that reduce emissions. CCS, SCR and scrubbers are examples of such technologies. This, in turn, can contribute to a more sustainable and environmentally friendly marine fuel sector.

6 Conclusion

Ammonia is one of the most widely produced chemical compounds in the world and is primarily utilized as a mineral fertilizer. Liquid ammonia has gained significant attention and has been increasingly adopted as a zero-carbon energy carrier in recent years. Blue ammonia is produced from natural gas or other fossil fuels with CCS and is heavily researched with its intention to work as a maritime fuel.

The flexibility in production methods makes it easy to switch to renewable sources compared to other marine fuels. This is putting ammonia at an advantage, since the overall emissions can be reduced substantially. Ammonia is a fuel that emits NO_x to a high degree through combustion. NO_x emissions are highly toxic, and implementations such as SCR in the engine is considered a necessity.

Ammonia can be used directly in an IC-engine with few or moderate modifications, like glow plugs or utilizing ammonia with a pilot fuel. Because of this, the threshold to replace traditional maritime fuels is lowered considering it reduces the necessity to make expensive modifications to the ship. Dual-fuel engines are considered a promising option for future ammonia usage.

Fuel cells are capable for both direct and indirect usage of ammonia. Fuel cells that are powerful enough for long-distance shipping are not available yet, and improvements are required before fuel cells can become a feasible and practical solution.

This case study compared HFO, blue ammonia, and biodiesel for the Mongstad-Reykjavik shipping route, with a specific focus on their life cycle analysis. The aim of the study was to evaluate ammonia as a marine fuel in terms of cost, emissions, and efficiency.

The results gained from the study, determined that blue ammonia produced from natural gas, emerges as the least sustainable option. It exhibits lower efficiency, higher emissions, and proves to be the most expensive fuel among the three. The market potential for ammonia as a maritime fuel relies on an increase in the price of CO_2 to compete with standardized marine fuels such as HFO and biodiesel.

Considering all the aspects of blue ammonia, it is evident that the production method must be done differently to cut down on emissions if it is to be implemented as a standardized marine fuel. Additionally, emission-reducing technologies should be implemented.

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A Classification of reciprocating engines

Class	Service	Approximate range of engine power (kW)	Predominant type		
			CI or SI	No. of strokes	Method of cooling
Road vehicles	Motor cycles, scooters	0.75–37.5	SI	2,4	A
	Small passenger cars	15–75	SI	4	A, W
	Heavy passenger cars	75–375	SI	4	W
	Light commercial	37.5–150	SI, CI	4	W
	Heavy (long distance) commercial	112.5–375	CI	4	W
Off-road vehicles	Light vehicles (Factory, airport, etc.)	1.5–15	SI	2,4	A, W
	Agriculture	3–150	SI, CI	2,4	A, W
	Earth moving	37.5–750	CI	2,4	W
	Military	37.5–1875	CI	2,4	A, W
Railroad	Rail cars	150–375	CI	2,4	W
	Locomotives	375–3000	CI	2,4	W
Marine	Outboard	0.4–75	SI	2	W
	Inboard motorboats	4–750	SI, CI	4	W
	Light naval craft	30–2250	CI	2,4	W
	Ships	3750–22500	CI	2,4	W
	Ships' auxiliaries	75–750	CI	4	W
Airborne vehicles	Airplanes	50–2600	SI	4	A
	Helicopters	50–1500	SI	4	A
Home use	Lawnmowers	0.75–3	SI	2,4	A
	Snow blowers	2–4.5	SI	2,4	A
	Light tractors	2–7.5	SI	4	A
Stationary	Building service	7.5–375	CI	2,4	W
	Electric power	40–22,500	CI	2,4	W
	Gas pipe line	750–3750	SI	2,4	W
Special for racing	Vehicles and boats	75–1500	SI	4	W
Toys	Model airplanes, autos, etc.	0.01–0.4	HW	2	A

Figure A.1: Classification of reciprocating engines by application. HW (Hot-wire ignition carburetted mixture), A (Air-cooled), W (Water-cooled) [69].

B Fure Valö ship info

Table B.1: Fure Valö ship info [128]

Name	FURE VALÖ
Type	Chemical/Oil products tanker
Main products	Chemicals
IMO-number	9739836
Call sign	SGTX
Flag	Sweden
Port of registry	Donsö
GT	12.770 t
DWT	17.991 t
NT	5.838 t
Length	149,90 m overall 146,64 m between perpendiculars
Breadth	22,80 m extreme
Draught	Max: 9,36 m
Freeboard	2.752 mm
Depth	12,10 m
Speed (max/average)	13,0/10,0 knots
Built	2018
Launch date	12/06/2018
Date of completion	27/11/2018
Builder	China Merchants Jinling Shipyard(Yangzhou)Dingheng Co.,Ltd. China
Yard number	AD0029
Hull material	Steel
Hull type	Double hull
Continuous decks	1
Main engine	1x Wärtsilä 9L34DF - 4 stroke single acting 9 cylinder 340 x 400 mm combustion engine 4.500 kW / 6.118 hp at 750 rpm Builder: Wärtsilä Finland OY
Propellers	1x Screw propeller controllable pitch
Boilers	1x CHM 235,00 m ² - 8,0 bar 1x CHO 64,00 m ² - 8,0 bar
Shaft generator	1x 2.250 kVA - 1.800 kW
Generators	1x Main diesel generatorset 856 kVA - 685 kW - 980 hp 1x Main diesel generatorset 2.000 kVA - 1.600 kW - 2.262 hp
Emergency generator	1x Diesel generatorset 250 kVA - 200 kW - 345 hp
Number of cargo tanks	12
Total capacity of tanks	20.216,5 m ³
Tank capacities	Fuel: 712,6 m ³
ISM & commercial manager	Furetank Rederi AB Korsholmebacke 1 SE-430 82 Donsö Sweden
Operator	Rederi AB Älvtank
Registered owner	Furetank Rederi AB Korsholmebacke 1 SE-430 82 Donsö Sweden
Latest data adjustment	26 September 2021

C MATLAB calculations

```
close all; clear ; clc
```

Fuel data

```
% Supply energy SE [MJ/kg]
SE_a = 18.6;

SE_HFO = 40.5;

SE_bio = 37.8;

% Density p [kg/m^3]
p_a = 682;

p_HFO = 1000;

p_bio = 875;

% Price [USD/kg]

P_a = 0.5;

P_HFO = 0.623;

P_bio = 1.49;

% Amount of CO2 emissions [kg CO2]

CO2_a = 48700;

CO2_HFO = 366000;

CO2_bio = 325000;

% Amount of NOx emissions [kg NOx/kg fuel]

NOx_a = 0.47;

NOx_HFO = 0.14;

NOx_bio = 0.048;
```

Other data

```

% Distance in truck
d_trans = 437; %km

% Diesel price
P_di = 1.753; %USD/L

% Amount of diesel per km in truck
m_di = 0.25; %L/km

% Distance on ship
d_ship = 1000*1852; %m

% Capacity truck storage
V_trans = 41.6; %m^3

% Capacity tank on ship
V_tank = 712.6; %m^3

% Average speed ship
v_ship = 5.45; %m/s

% Time estimate ship
t_ship = (d_ship / v_ship) /3600; %h
X = ['Shipping duration = ', num2str(t_ship), ' h'];
disp(X)

```

Shipping duration = 94.3935 h

```

% Cost NOx
P_NOx = 2.28; %USD/kgCO2

% Cost CO2
P_CO2 = 0.1; %USD/kgCO2

% Cost CO2 20% increase
P_L_CO2 = P_CO2 * 1.2; %USD/kgCO2

% Cost CO2 40% increase
P_M_CO2 = P_CO2 * 1.4; %USD/kgCO2

% Cost CO2 60% increase

```

```
P_H_CO2 = P_CO2 * 1.6; %USD/kgCO2
```

Amount of fuels Mongstad to Reykjavik

```
m_HFO = 100000; %kg
```

```
m_a = (SE_HFO*m_HFO)/SE_a; %kg
```

```
m_bio = (SE_HFO*m_HFO)/SE_bio; %kg
```

```
X = ['Amount ammonia = ', num2str(m_a), ' kg'];  
disp(X)
```

Amount ammonia = 217741.9355 kg

```
Y = ['Amount HFO = ', num2str(m_HFO), ' kg'];  
disp(Y)
```

Amount HFO = 100000 kg

```
Z = ['Amount Biodiesel = ', num2str(m_bio), ' kg'];  
disp(Z)
```

Amount Biodiesel = 107142.8571 kg

Truck

```
% Number of truck rides  
n_truck_a = ((m_a / p_a) / V_trans);  
Z = ['Number of trucks = ', num2str(round(n_truck_a))];  
disp(Z)
```

Number of trucks = 8

```
% Total distance for trucks  
d_tot_trans = d_trans * n_truck_a; %km  
Z = ['Total distance for transport = ', num2str(d_tot_trans), ' km'];  
disp(Z)
```

Total distance for transport = 3353.8668 km

```
% Total amount of diesel for truck  
m_tot_di = m_di * d_tot_trans; % L  
Z = ['Amount of diesel for transport = ', num2str(m_tot_di), ' L'];
```

```
disp(Z)
```

Amount of diesel for transport = 838.4667 L

```
% Cost for transportation of Ammonia  
C_di = P_di * m_tot_di; %USD  
Z = ['Cost of transportation for ammonia = ', num2str(C_di), ' USD'];  
disp(Z)
```

Cost of transportation for ammonia = 1469.8321 USD

Costs fuel

```
C_a = P_a * m_a; %UDS  
  
C_HFO = P_HFO * m_HFO; %UDS  
  
C_bio = P_bio * m_bio; %UDS  
  
x = categorical({'Ammonia', 'HFO', 'Biodiesel'});  
x = reordercats(x, {'Ammonia', 'HFO', 'Biodiesel'});  
C = [C_a C_HFO C_bio];  
bar(x, C)  
ylabel('Cost (USD)')
```

Cost NOx emissions

```
C_NOx_a = P_NOx * NOx_a * m_a; %USD  
  
C_NOx_HFO = P_NOx * NOx_HFO * m_HFO; %USD  
  
C_NOx_bio = P_NOx * NOx_bio * m_bio; %USD  
  
C_NOx = [C_NOx_a C_NOx_HFO C_NOx_bio];  
bar(x, C_NOx)  
ylabel('Cost (USD)')
```

Costs CO2 emissions today

```
C_CO2_a = P_CO2 * CO2_a; %USD  
  
C_CO2_HFO = P_CO2 * CO2_HFO; %USD  
  
C_CO2_bio = P_CO2 * CO2_bio; %USD
```

```

C_CO2 = [C_CO2_a C_CO2_HFO C_CO2_bio];
bar(x,C_CO2)
ylabel('Cost (USD)')

```

Total cost: CO2 emissions, NOx emissions, fuel costs and transportation

```

TC_a = C_NOx_a + C_CO2_a + C_a + C_di; %USD

TC_HFO= C_NOx_HFO + C_CO2_HFO + C_HFO; %USD

TC_bio = C_NOx_bio + C_CO2_bio + C_bio; %USD

TC = [C_a C_NOx_a C_CO2_a C_di; C_HFO C_NOx_HFO C_CO2_HFO 0;C_bio C_NOx_bio
C_CO2_bio 0];
bar(x,TC,'stacked')
ylabel('Cost (USD)')
legend('Fuel cost' , 'NOx cost' , 'CO2 cost', 'Transport')

```

Costs future with higher CO2 cost and SCR

```

% Today
CF_a = CO2_a * P_CO2 + C_a + C_di; %USD

CF_HFO = CO2_HFO * P_CO2 + C_HFO; %USD

CF_bio = CO2_bio * P_CO2 + C_bio; %USD

CF = [CF_a CF_HFO CF_bio];
bar(x,CF)
ylabel('Cost (USD)')

% 20% increase
CF1_a = CO2_a * P_L_CO2 + C_a + C_di; %USD

CF1_HFO = CO2_HFO * P_L_CO2 + C_HFO; %USD

CF1_bio = CO2_bio * P_L_CO2 + C_bio; %USD

CF1 = [CF1_a CF1_HFO CF1_bio];
bar(x,CF1)
ylabel('Cost (USD)')

% 40% increase
CF2_a = CO2_a * P_M_CO2 + C_a + C_di; %USD

CF2_HFO = CO2_HFO * P_M_CO2 + C_HFO; %USD

```

```
CF2_bio = CO2_bio * P_M_CO2 + C_bio; %USD
```

```
CF2 = [CF2_a CF2_HFO CF2_bio];
```

```
bar(x,CF2)
```

```
ylabel('Cost (USD)')
```

```
% 60% increase
```

```
CF3_a = CO2_a * P_H_CO2 + C_a + C_di; %USD
```

```
CF3_HFO = CO2_HFO * P_H_CO2 + C_HFO; %USD
```

```
CF3_bio = CO2_bio * P_H_CO2 + C_bio; %USD
```

```
CF3 = [CF3_a CF3_HFO CF3_bio];
```

```
bar(x,CF3)
```

```
ylabel('Cost (USD)')
```

