SHORT STUDY

Ammonia as ship fuel

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EXECUTIVE SUMMARY

The short study "Ammonia as Ship Fuel" aims to give a comprehensive overview of a possible conversion of a cargo ship to ammonia as main fuel. The approach considers an evaluation of the basic fuel characteristics and literature to derive a first projection of the performance and emissions of an ammonia energy conversion system. A concept ship design is created to clarify the essential shipbuilding aspects, namely an information on the arrangement of ammonia storage, exhaust gas after-treatment, bunker station as well as safety areas. Finally, we evaluate the carbon footprint of Ammonia for several production routes and take into account the use as marine fuel.

The results show that ammonia is attractive due to the higher energy density compared to hydrogen while still combusting CO_2 free. However, ammonia's toxicity, reluctance to combust and the nitrogen chemistry affecting NO, NO_2 and especially N_2O emissions are to be considered and will require more complex technical solutions.

As Ammonia has a low energy content compared to diesel it will always require larger tanks for storage. Therefore, a vessel designed for using ammonia as primary fuel compared to a vessel using conventional fuels will always either be larger or have a decreased cargo capacity or range. Considering the special needs of alternative fuels and Ammonia in particular, there has to be a holistic approach in optimizing the vessel design, entirely. The vessel design, starting with tank arrangement, special dedicated exhaust gas aftertreatment equipment, safety areas, the use of specific material, need to be reconsidered.

From a carbon footprint perspective, synthetic Ammonia has the potential to reduce greenhouse gas (GHG) emissions for both production and utilization as an alternative marine fuel. To achieve these GHG emission reductions, low-carbon electricity sources based on renewable energies and grid mixes with a large share of renewable or nuclear electricity are needed. Thereby, synthetic Ammonia enables the integration of renewables into the chemical industry and the transportation sector. If Ammonia from renewable electricity fully substitutes conventional marine fuels as well as conventional ammonia production for chemical use, the additional (renewable) electricity demand corresponds to up to 5 % (chemical use) and 14 % (marine fuel use) of curent global electricity generation. However, besides the carbon footprint, other environmental impacts need to be considered based on detailed production and engine-related emission data for a full life-cycle perspective.

Our rough cost estimation shows a strong dependence on hydrogen price, i.e., electricity price. Synthetic Ammonia can only be competitive to conventional marine fuels with cheap hydrogen or if a fossil carbon tax is added to the conventional marine fuel. Our cost estimate should be expanded to include both infrastructure and ammonia transportation costs.

Based on the results of the study, we are confident that a solid base for a continuation is set. Working in close cooperation with researcher, operator, classification societies and suppliers would be beneficial in developing a respective concept design and a pressing need is unavoidable in view of the climate change, and to reduce the carbon footprint.

CONTENTS

① INTRODUCTION

The short study "Ammonia as Ship Fuel" is divided into four main topics:

A | The basic fuel characteristics (Section 2) are discussed: reactivity and related hazards for humans, environment, and materials, as well as application-related fuel properties and nitric oxide formation during ammonia oxidation.

B | An evaluation of possible energy conversion systems for ammonia as a fuel. The main focus will be internal combustion engines, but fuel cells and turbines will be touched upon. The options of an NH_3/H_2 mixture for large engines will be considered, as well as the transferability of operation with diesel as ignition fuel from 2-stroke to 4-stroke engines. A first projection of a possible performance and emission characteristic for the LCA will be given (Section 3).

C | A rough ship design, to clarify the essential ship-building aspects, has been developed (information on the arrangement of ammonia storage, exhaust gas aftertreatment, bunker station as well as safety areas). The necessary drawings have been evaluated together with a classification society and initial clarifying discussions with other classes or possibly also flag states have been initiated. An idea on essential safety aspects will be given accordingly (Section 4).

D | Finally, the carbon footprint is assessed for several ammonia production pathways, including conventional and green ammonia (cradle-to-gate). The supply of the needed inputs for green ammonia production (e.g., electricity, nitrogen) are investigated, and a sensitivity study is performed. Including the emission results of Section 3, ammonia is assessed from cradle-to-grave and benchmarked to conventional marine fuels in terms of emissions and costs (Section 5).

② FUEL PROPERTIES

2.1 REACTIVITY AND CORRESPONDING HAZARDS FOR HUMANS, ENVIRONMENT, AND MATERIAL

The health hazard of ammonia is classified as extremely dangerous in the NFPA 704 [1] (also called the fire diamond). Typical injuries due to exposure with ammonia include inhalation and direct skin or eye contact. However, the smell of ammonia is detectable for humans at concentrations above 5 ppm. Also, ammonia does not act as a nerve agent which reduces the risk of overexposure. The 8-hour safety limit is 20-25 ppm, while severe health effects are observed form 300 ppm and the lethal concentration is 5000 ppm or higher [2].

The fire hazard is relatively low due to the high flash point of 132 °C. Also, the physical and chemical stability of ammonia posses no risk for explosions [2]. However, ammonia is classified as corrosive in the NFPA 704.

The above-mentioned hazards pose challenges for application of ammonia. Especially leakages of ammonia must be avoided with technical solutions to reduce the risk to life in the surroundings. Also, the selection of materials that are in frequent contact with ammonia needs to be carefully considered. These risks and challenges are managed for many years already though as ammonia is one of the chemicals that is traded in the largest quantity worldwide mainly for its use in fertilizer production. Therefore, safety and material compatibility studies are available in the literature, e.g., [3].

For materials often used in large bore engines that are powering most of the ships currently on the seas, the compatibility is listed in the following. The section is based on multiple material compatibility tables that are available in the literature, e.g., [4], [5], [6], [7]. For ferreous metals, corrosion is mainly driven by impurities (sulfates, chlorides, …). One mechanism that is potentially causing damages is stress corrosion cracking. Here, the Ammonia is nitrating the surfaces over time. The hardened material is then more prone to crack. This effect can be prevented by adding water to ammonia. With some water added, a good compatibility is observed with cast iron and carbon steel. Highly alloyed steels can however perform worse and nickel contents over 6 % should be avoided. Contrarily, aluminum performs best for anhydrous ammonia. Therefore, mixing ferreous materials and aluminum is not recommended. Also, direct contact of ammonia to bearing materials like copper must be avoided. Moreover, the compatibility with plastics is to be checked, but there are many plastics available that are suited well for usage with ammonia.

In summary, ammonia posses many challenges for the safety system due to its hazards to human health and in terms of its corrosivity towards many standard materials. As the experience with ammonia in the chemical industry was built for many decades by now, these challenges can today be considered as manageable in a professionalized environment as e.g., shipping.

Some general fuel properties of ammonia in comparison to diesel and other alternative fuel candidates are summarized in Table 1. Starting with the lower heating value, ammonia has the lowest value depicted. This value is comparable only to methanol. The gravimetric energy density of these candidates is less than half that of diesel fuel.

	Diesel / MGO (liq.)	Methanol (liq., 65°C)	Ammonia (liq., -33°C)	LNG (Methane) (liq., -162°C)	Hydrogen (liq., -253°C)	LPG (Propane) (liq., -42.4°C)
Lower Heating Value (in MJ/kg)	42.7	19.7	18.6	50	120	46.4
Mixture Heating Value (DI) (in MJ/m³)	3.8	3.92	3.92	3.76	4.54	3.82
Fuel tank size relative to MGO*	1.0	2.3	2.8	1.7	4.2	1.3
Adiabatic Flame Temperature (in °C)	2030	1880	1800	1950	2110	2000
Ignition Temperature (in °C)	≥ 225	440	630	595	560	470
Lower / Upper Flammability Limit (Vol.-%)	0.6 / 6.5	6 / 50	14 / 32.5	4.4 / 17	4 / 77	1.7 / 10.8

*Table 1: Fuel Properties of ammonia and other alternative fuel candidates compared to diesel (*fuel tanks size only considers fuel volume; Sources: [8], [9], [10], TME)*

Still, all fuels are mostly comparable in terms of the mixture heating value in case of direct fuel injection. This leads to a similar amount of energy released per air mass. Therefore, in theory all the fuel options allow for a similar power density of the propulsion system.

The energy density is however evident in the fuel tank size that is only considering the fuel volume here. Gaseous fuels are assumed to be liquefied (cryogenic storage). While methanol as the only liquid alternative fuel listed already requires 130 % more volume for the same energy content, this value raises to 180 % for ammonia and to 320 % for hydrogen. As can also be seen in Figure 1, hydrogen requires a temperature of -253 °C to be liquefied, while -33 °C is sufficient for ammonia. This will have a significant impact on the insulation required. Another option for ammonia is a pressurized storage at pressures known e.g., from LPG passenger cars (< 10 bar).
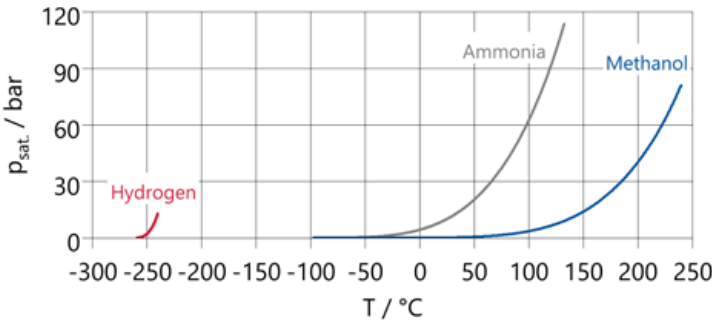

Figure 1: Saturation pressure for hydrogen, ammonia, and methanol (Source: [8])

Ammonia has the lowest adiabatic flame temperature depicted in Table 1. In theory, this should be beneficial for the NO_X emission formation. However, as nitrogen is bound in the fuel, there are side effects for the NO_X and the N_2O formation. This will be discussed in detail in the section 2.3.

The ignition temperature is the highest and the flammability limits are the narrowest for ammonia compared to the fuels in Table 1. Ammonia is reluctant to combustion and requires special measures to allow an efficient and clean combustion. Looking at the ignition delay times depicted in Figure 2 shows the longest values at a certain temperature for ammonia. This is beneficial to suppress anormal combustion in otto cycle engines. Considering dimethyl ether as a reference for a diesel-like fuel with a cetane number of 60 shows that diffusive combustion of ammonia will only be possible with supportive measures as e.g., a pilot diesel injection to preheat the combustion chamber.
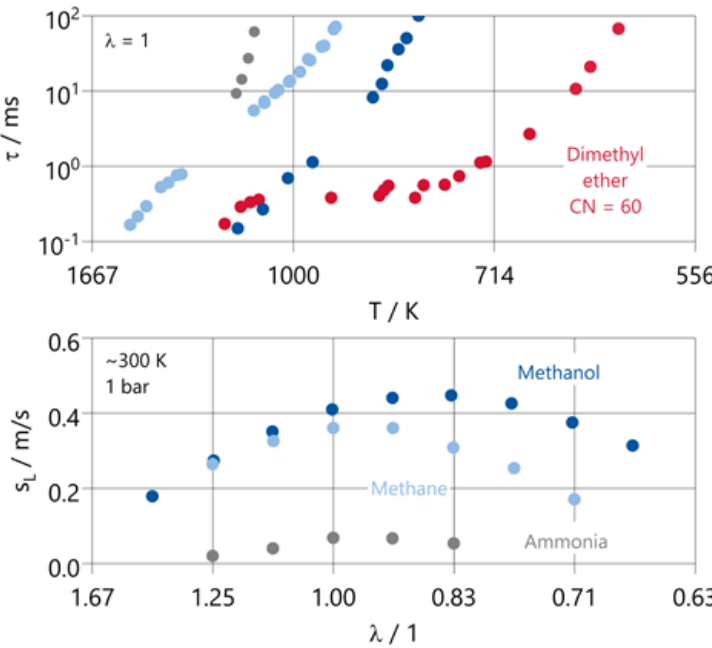

Figure 2: Ignition delay times and laminar flame speeds for hydrogen, ammonia, and methanol (Source: [11], [12], [13], [14], [15], [16], [17])

Finally, the laminar flame speeds in Figure 2 reflect what was also evident in the flammability limits. Ammonia is reluctant to burn and requires high temperatures for combustion. Hence, regardless of the combustion system of a large bore ammonia engine, supportive measures to either increase the flame speed for otto cycle combustion or to elevate the temperatures for diffusive combustion are required. Combustion but also other possible applications of ammonia for energy conversion will be discussed in more detail in chapter 3.

2.3 NITRIC OXIDE FORMATION DURING AMMONIA OXIDATION

For oxidation of conventional fuels, the NO formation can be described with the Zeldovich mechanism. Mainly, high temperatures are required to initiate the breakup of the stable N_2 molecule:

$$N_2 + O \leftrightarrow NO + N \ (1)$$
$$N + O_2 \leftrightarrow NO + O \ (2)$$
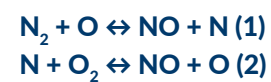
The second factor is the availability of oxygen. The described influences lead to a peak in the NO_x formation for relative air fuel ratios (rel. AFR) close to stoichiometric in lean conditions. The leaner the mixture is, the lower the peak combustion temperatures will be. As a result, after the peak at rel. AFR ~1.1, the NO_x concentration is reduced. Contrarily to this behavior, ammonia forms fuel NO_x in addition. Here, the influence of the temperature level on NO_x formation differs significantly from conventional fuels. Nitrogen based radicals and atomic nitrogen are present in the reaction pathway of NH_3 leading to fuel derived nitric oxides. Oxygen availability remains a significant parameter for the NO_x formation though [18]. As nitrogen-based radicals are available at all rel. AFRs, lean operation will likely never lead to a reduction in NO_x emissions. For a limited rel. AFR range, this is shown in Figure 3.
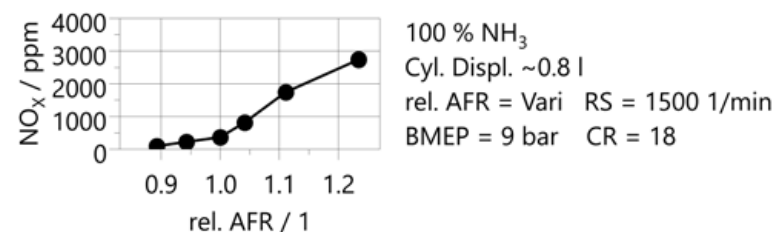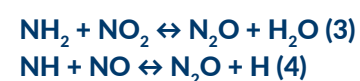

Figure 3: NO_x emissions over the rel. AFR for pure ammonia SI combustion (Source: [19])

Like NO, N_2O is also in the oxidation path of ammonia. N_2O is primarily formed via:

$$NH_2 + NO_2 \leftrightarrow N_2O + H_2O \ (3)$$
$$NH + NO \leftrightarrow N_2O + H \ (4)$$

There is a peak in the N_2O concentration in stoichiometric conditions at ~1300 K. This is shifted to lower temperatures with increasing oxygen concentration (~1150 K at rel. AFR = 2) [18]. Hence, high temperature combustion might be mandatory for ammonia to avoid excessive N_2O concentrations. N_2O is a greenhouse gas with a GWP_{100} of ~300.

Ammonia is not only discussed as a fuel but also as a potential hydrogen carrier enabling easier transportation and storage. Ammonia decomposes at high temperatures (> 600 °C). The temperature threshold can be reduced to ~400 °C with modern catalytic materials [20]. However, the reaction is endothermic and the heating value / enthalpy flow of the produced H_2 is increased by 14 % compared to the ammonia input stream. Hence, a heat source is required which limits the transient operability and reduces the mobility of an Ammonia cracking system. Still, this concept can work fine depending on the purity required for the specific application. This is summarized in Figure 4.

Polymer electrolyte membrane (PEM) fuel cells have stringent H_2 purity requirements. This does not suit the option of an on-board conversion of NH_3 to H_2 well, as a small residual NH_3 fraction requires significant technical efforts to be undertaken. Alkaline fuel cells can cope with much higher residual NH_3 shares though. Research for low temperature direct ammonia fuel cells (DAFC) is ongoing (see e.g., [21]). Solid Oxide Fuel Cells (SFOC) can operate on pure ammonia. However, the membrane can degrade quickly with pure NH_3 feed, and a catalytic decomposition seems sensible also for SFOCs [22].
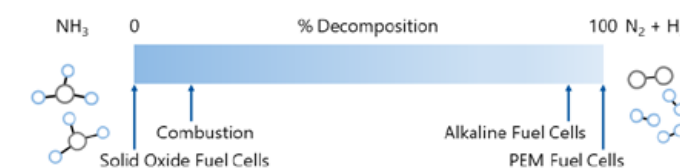

Figure 4: Required purity of H_2 cracked from ammonia for different applications (Source: [23])

Besides SOFCs, also combustion applications can work with high shares of ammonia. In Japan, research is ongoing for co-firing of coal power plants with ammonia, see [24]. Also, ammonia powered gas turbines are being investigated, see [25]. Here, burner technology must be adapted for pure NH_3, but current gas turbines could be operated on a blend of ammonia and natural gas or hydrogen.

Besides these technologies, ammonia can also be converted to mechanical energy utilizing internal combustion engines. As these are the main propulsion system for shipping, the next section will go into detail on the options and a possible solution for conversion of the targeted F-Type vessel.

3.1 AMMONIA COMBUSTION IN INTERNAL COMBUSTION ENGINES

Ammonia was used as a bus fuel in Belgium during the second world war due to shortage of fuel. Besides this, the number of applications for ammonia as a fuel for internal combustion engines is limited currently. That said, there still are studies available in the literature that have investigated the combustion of ammonia in different combustion systems.

E.g., Niki [26] and Reiter [27] have investigated the fumigation of a diesel engine with ammonia in the intake port. Duynslaegher [19] has investigated premixed SI combustion of pure ammonia with a relatively high compression ratio (15-19). Hence, operation with pure ammonia fed to the port of an internal combustion engine is possible. However, e.g., for the premixed combustion system investigated by Duynslaegher [19], the compression ratio must be optimized to enable both low load operation and still stay clear of the PFP or knock limit at high loads.

Rouselle [28] has investigated the minimum load on ammonia in a modern gasoline engine with a compression ratio of 10.5 and found that idle operation is not possible on pure ammonia. Toyne [29] has presented a tractor that feeds some H_2 to the port as well on a SI engine to enable a safe startup. The NH_3 share in warm operation is 85-90 %. Hence, if ammonia shall be burned with a low-pressure injection in the port as a premixed charge, a flame speed enhancer or other supportive measures will be required to prevent excessive NH_3 but also N_2O emissions at least at low loads.

All the mentioned investigations were performed on relatively small engine geometries. The targeted F-Type vessel however has a six-cylinder medium speed engine with a power output of 5.4 MW. Due to the reluctance to combust that ammonia shows, an alternative approach is selected for this study. A pilot diesel assisted diffusive combustion system is selected for the life cycle analysis. Although there are no results available on such a combustion system, the Stena Germanica ferry is in operation with such a combustion system since 2015, however fueled with methanol. Also, the chair of thermodynamics of mobile energy conversion systems (TME) has experience with such a combustion system with methanol (see e.g., [31], [32], [33]).

Moreover, Gross [30] has investigated ammonia DME blends. DME is a gaseous fuel with a similar saturation pressure as ammonia that has a diesel like ignition characteristic. The results do not show a suppression of the ignition of the diesel-like fuel by ammonia and hence provide confidence for the application of ammonia in pilot assisted combustion systems. In addition to these hints, MAN ES has announced to develop an ammonia version of its ME LGI engine, which uses this type of combustion in the two-stroke cycle. Also, in AmmoniaMot MAN ES wants to develop a four-stroke medium speed ammonia engine utilizing a similar technology.

3.2 AMMONIA INTERNAL COMBUSTION ENGINE AND AFTERTREATMENT SYSTEM

To ensure ignition also in cold start conditions, pilot diesel injection support is the most attractive option to lead to the subsequent autoignition of ammonia in a diffusive combustion system. This however requires direct injection of two fuels – dual direct injection (DDI). The concept will be called DDI CI in the following, as both fuels are injected directly into the combustion chamber and both fuels are compressed to ignite. As a diffusive combustion system, the scalability is superior, and the exact bore diameter of the engine finally chosen for conversion is of secondary importance. Figure 5 depicts the phases of DDI CI combustion with a possible layout of the combustion chamber.
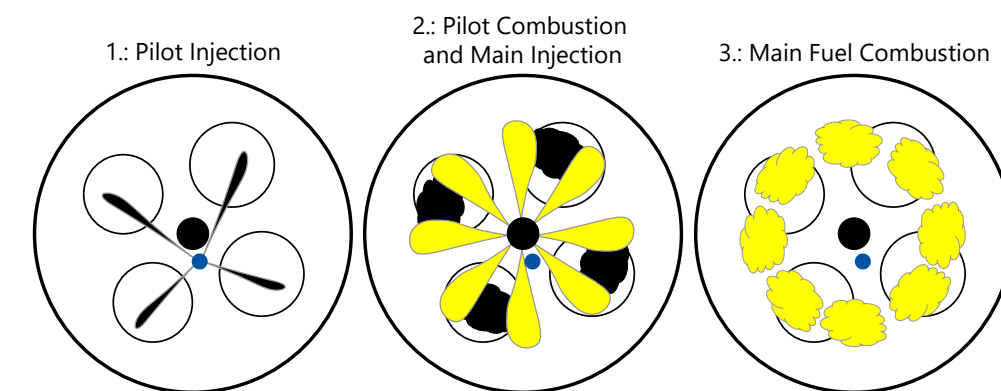

1.: Pilot Injection   2.: Pilot Combustion and Main Injection   3.: Main Fuel Combustion

Figure 5: Phases of DDI CI combustion (Source: [32]; Methanol can be replaced with Ammonia)

Initially, a diesel pilot injection is performed shortly before TDC. Once the spray plumes have ignited, the main ammonia injection starts. The ammonia spray plumes in the area where the diesel has combusted ignite first and increase temperature and pressure. This subsequently leads to ignition and combustion of all ammonia spray plumes.

While the overall working principle can be taken over from methanol to ammonia as a main fuel since many fuel properties are similar, the ignition and realization of complete ammonia combustion require some adaptations (compare ignition delay times). As the pilot diesel share is both thermodynamically disadvantageous and leads to CO_2 emissions, it shall not be increased to enable stable operation. To still support the stable combustion of ammonia, the compression ratio can be elevated. The effects are shown in Figure 6.
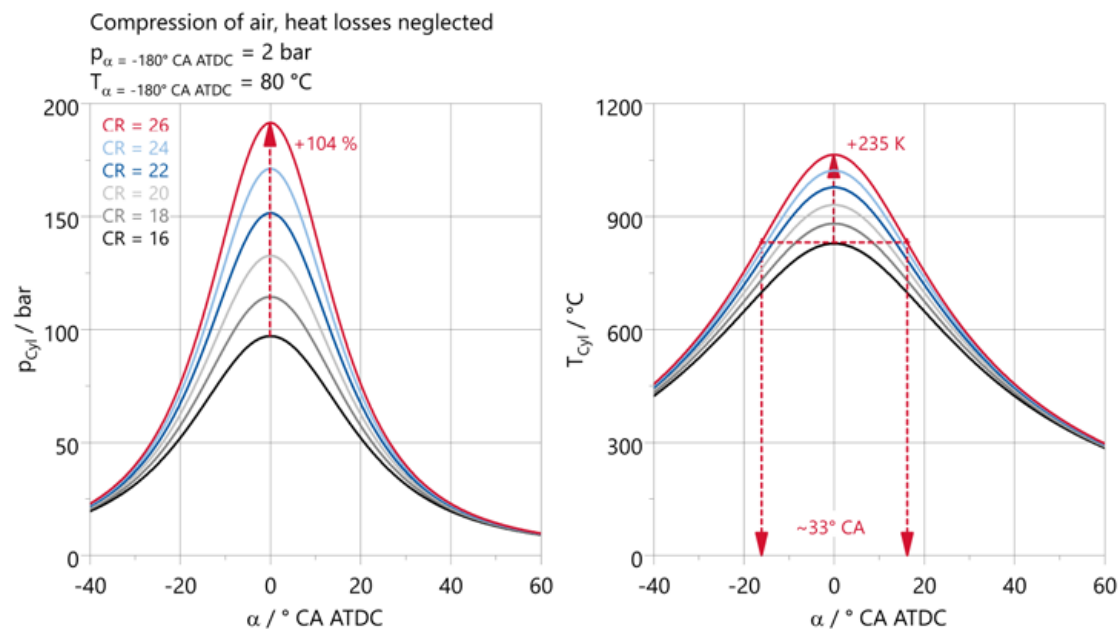
Figure 6: *Influence of increasing compression ratio*

Figure 7: *Power density and resulting cylinder configuration of the engine*

With increasing compression ratio, the compression end pressure increases and consequently also the peak firing pressure. While this is disadvantageous for the power density, it also increases the compression end temperature. This widens the time window with sufficient temperature for oxidation. The combination of a higher pressure and temperature improves the ignitability of an ammonia injection and hence limits the support required by a pilot diesel injection.

As mentioned, the higher compression ratio limits the maximum load and, hence, the power density of the engine. This is summarized in Figure 7. The left diagram shows the required BMEP for different cylinder configurations to match the power output of the original engine. The diesel engine on the F-Type vessel is a MaK M43C six-cylinder engine with a maximum BMEP of 24.4 bar. The ammonia engine is assumed to be based on the Dual Fuel variant for this engine, the M46DF which is a natural gas dual fuel engine. This engine has an increased bore diameter of 460 mm compared to 430 mm as

is common for natural gas dual fuel engines to maintain the power output at lower specific loads. The considerations are focused on the mentioned MaK engines, but are still applicable to similar designs. Due to the larger bore diameter, the BMEP of an equal power output to the 6M43C diesel engine is lower for an identical number of cylinders. The dual fuel variant is however selected for the modified cylinder head design. Usually, a main and a pilot injector are already implemented for such an engine limiting the effort for conversion. Outer dimensions of the engines usually stay similar.

Besides this adaption of the base engine, an adapted combustion calibration is assumed for ammonia. While diesel engines usually retard the injection timing at full load to reduce the peak firing pressure, this is limited for ammonia due to the reduction in temperature during the expansion stroke (compare Figure 6). Therefore, the maximum compression end pressure is reduced from 220 bar for diesel to 180 bar for ammonia.
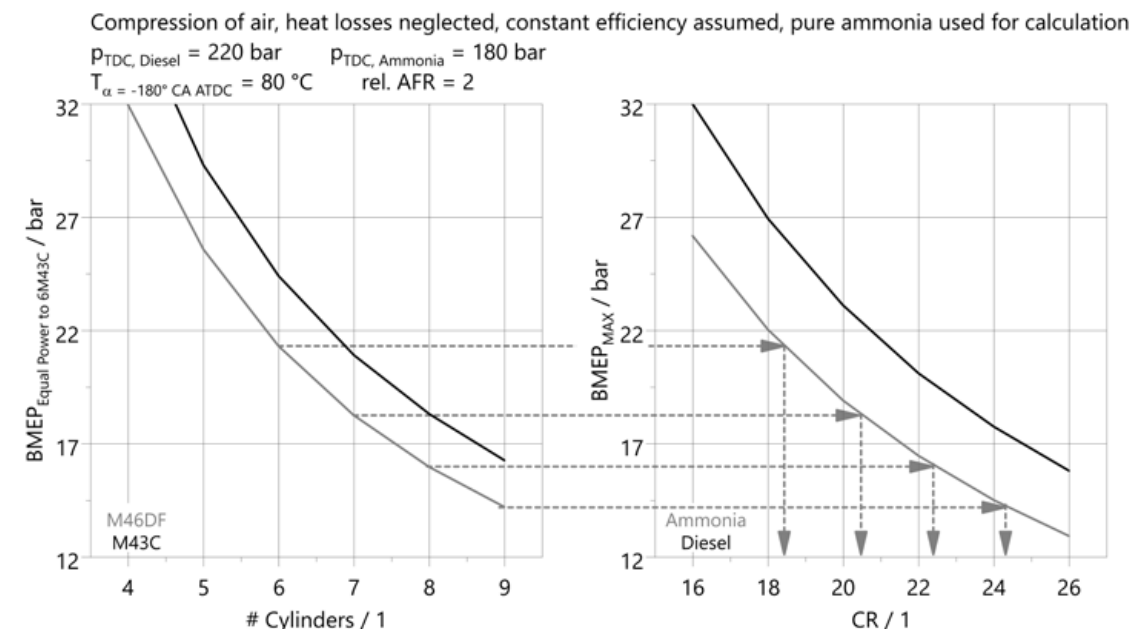
The righthand side of the figure shows the maximum possible compression ratio for different cylinder configurations to stay clear of the peak firing pressure limit. For a six-cylinder engine, this would result in a BMEP of about 21 bar and a compression ratio slightly above 18. Since the compression ratio shall be increased to reduce the pilot diesel share, an inline 8-cylinder configuration is selected to set achievable targets of a BMEP in the range of 16 bar with a compression ratio of 22.5. This measure

would increase the length of the engine by 1.5 m or about 20 %.

Besides the increased cylinder count, additional space should also be reserved for the exhaust gas aftertreatment system. The system layout is shown in Figure 8. As the emission levels for N_2O and NO_x are very uncertain at this point, the shown aftertreatment layout represents a very conservative first estimation.
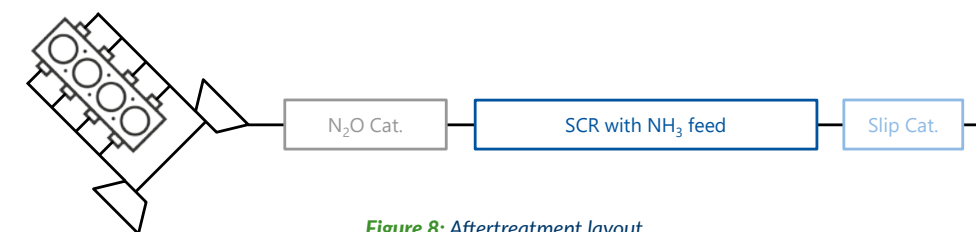

Figure 8: *Aftertreatment layout*

Although the diffusive combustion at high temperatures and without significant fuel slip should lead to low N_2O emissions, a N_2O catalyst is implemented after the turbine. N_2O catalysts are applied in the industry, see also e.g., [34], [35] for insights. A volume like a conventional diesel SCR system is assumed making the estimation very conservative.

The SCR system will work with direct NH_3 feed. The substrate is assumed to be three times as large as for the standard diesel engine to cope even with unrealistically high NO_X emission levels. Finally, the slip catalyst is also scaled up significantly.

These deliberations lead to a first projection of the performance and emissions for such an ammonia engine. The 6M43C baseline is not derived by test data from MaK but is assumed based on experience at TME. All deliberations for the ammonia engine are relative to the diesel engine to ensure a fair comparison. Three estimates for the ammonia engine are depicted in Figure 9.
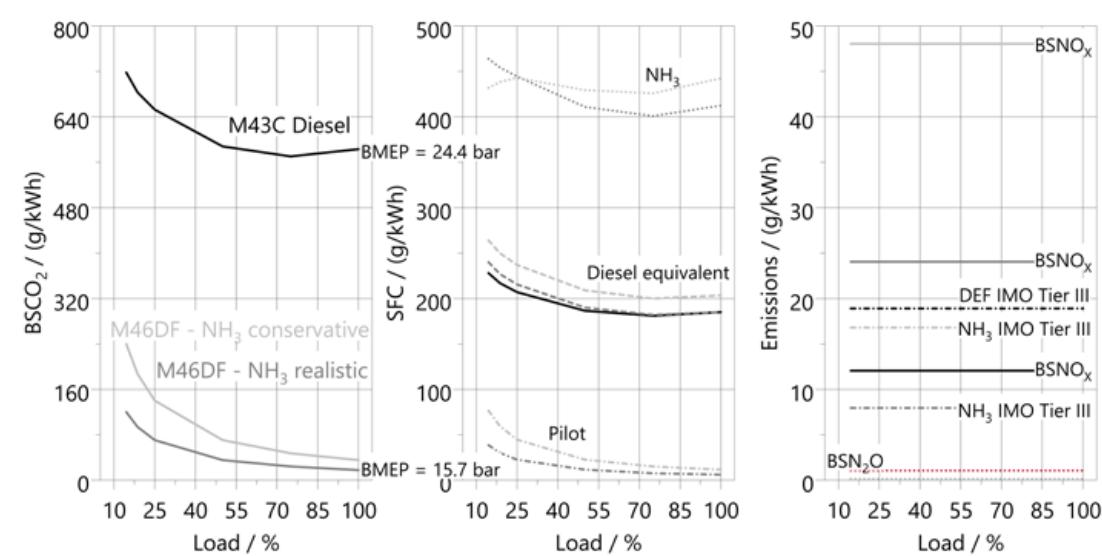
Scenario one is depicted in dark grey. A pilot diesel share of 3 % by energy is assumed for full load operation. The quantity is maintained over the load range. The diesel efficiency is assumed to be met at full load. NO_X emissions are assumed to be twice the diesel level and BSN_2O is taken into consideration with 0.1 g/kWh.

The second scenario is depicted in light grey. Here, twice the diesel quantity is assumed to be necessary. Efficiency is 10 % below the diesel level, while NO_X emissions are quadrupled. BSN_2O is also assumed to be 0.1 g/kWh.

The third scenario assumes BSN_2O emissions of 1 g/kWh, while all other values are identical to scenario one.

In all cases, the NO_X emissions are reduced with a NH_3 (or diesel exhaust fluid (DEF) in case of diesel) feed to meet the IMO Tier III standard.

Although the results shown in Figure 9 currently are only assumptions and a best guesses based on experience with other alternative fuels and ammonia investigations on much smaller engines, more results will likely be available in the years to come. Ammonia is coming up as a fuel currently. The announcements for new ammonia related projects, being its production or its usage for energy conversion systems, are growing exponentially. Besides MAN, also Wärtsilä and WinGD have announced plans to introduce ammonia engines in the near future. A comprehensive overview on ammonia related topics is provided by e.g., ammoniaenergy.org.

Still, the best guess in Figure 9 can serve as a valid input for the LCA to evaluate the ammonia value chain in this early state.

④ SHIP DESIGN

Within this section the focus was laid on a typical vessel, which is widely used by many ship owners. This MPV with heavy lift capacity has been proposed by one of the partners within the study framework.

The so called "F-Type" vessel was in a first instant considered as a conversion project. Herewith it was tried to check the possibility of a refit and the respective impact on the basic vessel.
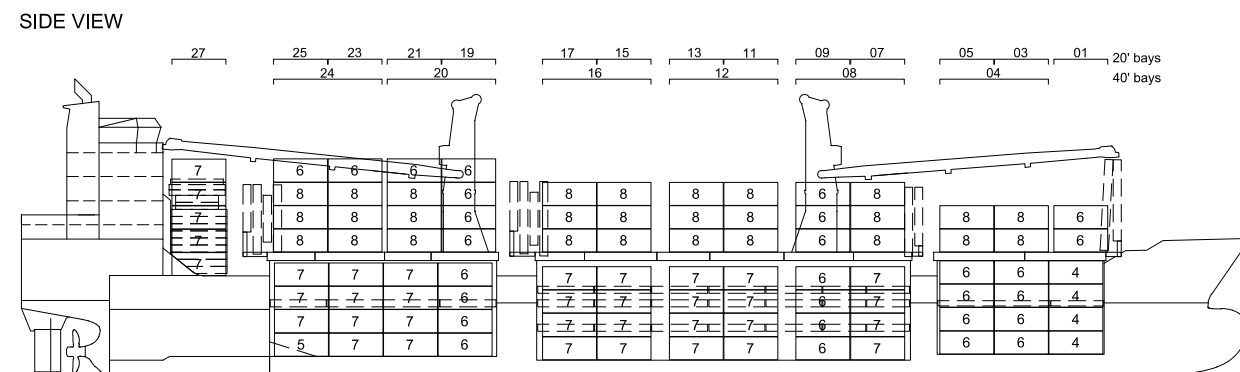
SIDE VIEW

Figure 10: General Cargo F-Type Vessel

The initial design has been scanned and the main characteristics like cruising range, speed and engine type has been taken as a basic requirement for a potential "Ammonia-F-Type". In a second step the advantages of a newbuild vessel and the main topics on that have been checked and highlighted.

The main framework for the regulatory evaluation has been the whitepapers from ABS "Ammonia as Marine Fuel" from October 2020, from DNV "Ammonia as a Marine Fuel" from November 2020 and the tentative rules set from BV "Ammonia

fueled Ships", NR671 DT R00 E from July 2021.
As a matter of fact, the IMO IGF- as well as the IGC-Codes are still considered as valid for most of the flag states and been used as a main requirement for ammonia as well. A respective working group on alternative fuels is actively working on a revision towards alternative fuels. A HAZID/risk assessment has to be performed for the individual vessel and it has to be proven that these fuels meet the intent of the goal and functional requirements concerned and provide an equivalent level of safety.

4.1 TWO STORAGE OPTIONS FOR NH$_3$ ON SEA-GOING VESSELS

There are currently two options to store ammonia on sea-going vessels:

Option 1
IMO Type A independent tanks which are fully refrigerated (around -33°C, close to ambient pressure), having a superb space utilization.

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A complete secondary barrier as well as a pressure and temperature control system is necessary. As a matter of fact, those have the highest energy demand for pressure and temperature control.

Option 2
IMO Type C independent tanks which are either semi-refrigerated (typically between 4 and 9 bar) or fully pressurized (approximately 18 bar).

The semi-refrigerated tanks need no secondary barrier. There is a pressure and temperature control system necessary as well but with a lower energy demand. The fully-pressurized tanks have the worst space utilization but also here, no secondary barrier

as well as no pressure and temperature control system are necessary. Furthermore no energy demand for pressure and temperature control are needed, but they are heavy and material intensive.

Converting the existing structural MGO-tanks of the vessel to IMO Type A tanks, is a theoretical option only. This may become an opportunity on smaller tanks and vessels with a lower range. For the studied case an IMO Type A tank and an IMO Type C tank (0°C, MARS 5 bar(a)) have been considered as a basis. Considering the energy density of ammonia, compared with marine gas oil (MGO),

a tank volume of three times higher than the MGO capacity is needed. This equals to about 3.350 m³ for Ammonia, taking the same operational profile into account. Beside that the necessary pilot fuel needs to be considered as well. To accommodate the ammonia fuel tanks with this volume the entire third cargo hold for a Type A tank as shown in figure 11.
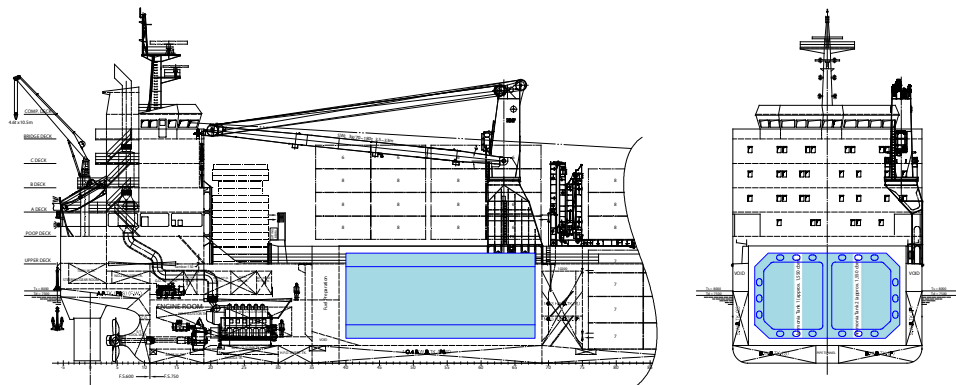

Figure 11: Type A Tank of about 3.350 m³

If type C tanks are being used, the on-deck stowage would need to be blocked by tanks additionally, see figure 12.
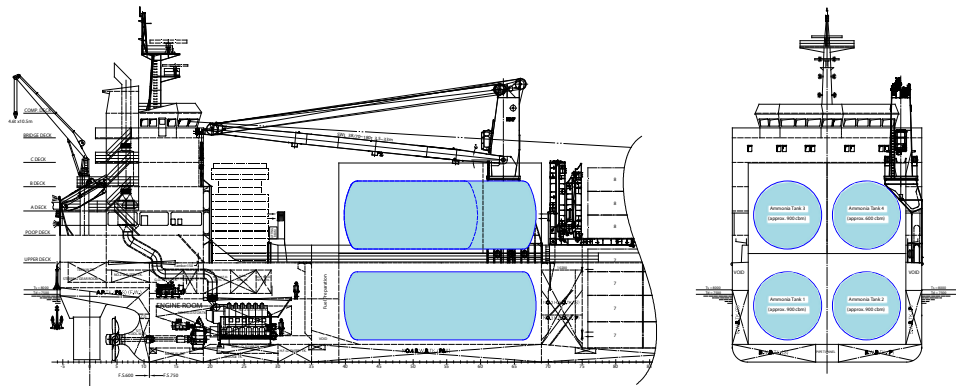

Figure 12: Type C Tanks of 3.350 m³

Additional technical rooms for fuel preparation and e.g. SCR or N_2O catalyst need respective space and must be integrated in the existing arrangement as well. It is needless to say that the refit under those conditions is commercially (OPEX and CAPEX) not feasible. An ammonia refit for an equivalency of about 1,100 m³ MGO is not reasonable, as long as a reduction of the endurance or more frequent bunkering is not acceptable and manageable.

Another alternative option has briefly been checked: installing ammonia tanks in front of the deck house

to minimize the cargo stowage impact. Following idea would need to be considered as well: The endurance is to be reduced to abt. 20% of actual design and the toxic ammonia is stored in direct vicinity of the accommodation. The handling of the hazardous zones is possible but challenging and the tank protection against damages during cargo operations is of high importance. In case of IMO Type A tanks, a complete housing would be needed and, very important, the centre of gravity (COG) is affected negatively.

4.2 ALTERNATIVE

As an alternative approach and disregarding the design of the example vessel, a much better realization approach can be seen on a vessel with its deck-

house in front. Hence, it is possible to overcome a certain part of the storage problem of the ammonia and the cargo stowage could be maximized as well.
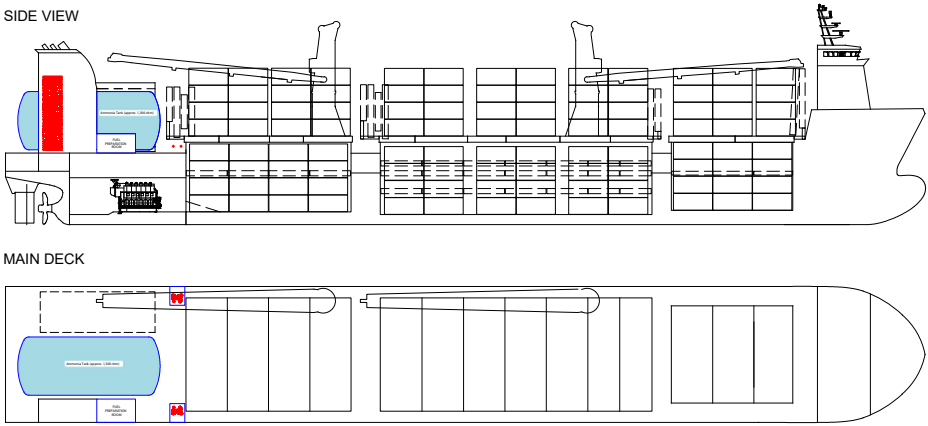

Figure 13: Alternative Vessel Design

In Section 5, we evaluate the carbon footprint and costs of ammonia as an alternative marine fuel. The carbon footprint is assessed based on the method life-cycle assessment (LCA). LCA is a holistic methodology for the environmental assessment of products and services, taking into account their entire life cycle [36, 37, 38]. The life cycle contains all activities from cradle-to-grave: from the extraction of raw materials, transportation, production, and product use, to recycling and final disposal of waste.

All flows of energy and materials exchanged with the environment throughout the life cycle are collected and interpreted regarding their environmental impacts. Various environmental impact categories such as climate change and acidification are usually considered. A detailed description of the LCA methodology is provided by the ISO 14040 and 14044 [36, 37]. Further, a simple cost assessment is performed.

In LCA, product systems are compared based on a so-called functional unit. The functional unit quantifies the function of the investigated product system and serves as a basis for comparison. To compare the carbon footprint of ammonia to conventional marine fuel, we use the functional unit "1 kWh$_{mech}$ (mechanical) used in a ship" (Figure 14). Hence, this functional unit captures the ultimate purpose: providing marine transportation.

For ease of interpretation, the alternative ammonia production routes are compared and benchmarked to the fossil route based on the functional unit of "1 kg NH$_3$" (Figure 14). Since the rest of the life cycle would be equal for all production routes, the cradle-to-gate boundaries are sufficient. Using this functional unit, we can determine the most favorable ammonia production route – regardless of ammonia's potential utilization as a fuel or chemical.

5.1 GOAL AND SCOPE

Currently, several routes are discussed in literature for the production of ammonia [40, 41, 42, 43, 44, 45]. LCA studies are available for ammonia production via the conventional Haber Bosch synthesis with carbon capture and storage (CCS)[46, 48, 50, 51] and by using hydrogen from biomass gasification [47, 48, 49, 50, 51]and water electrolysis. LCAs for ammonia utilization were conducted for vehicles [52] and the combustion with methane [53]. In this work, we perform a carbon footprint analysis based on LCA for ammonia production pathways with the subsequent utilization as marine fuel to cover the full life cycle. To identify the most favourable route from GHG emission perspective, we define the first goal of our study:

❶ Comparing the carbon footprint of several alternative ammonia production routes

In a second step, we extend our study to estimate the performance of ammonia as marine fuel by the second goal:

❷ Potential GHG emission reduction and costs utilizing ammonia as a marine fuel

Based on the two goals of our LCA study, we distinguish between cradle-to-gate and cradle-to-grave system boundaries for the benchmark (fossil-based product system) and the alternative product system Figure 14). The cradle-to-gate system boundary includes all processes associated with the production of ammonia.

The cradle-to-grave system boundary further comprises the subsequent utilization as a marine fuel. The GHG emissions due to factory construction for the alternative ammonia routes are neglected due to the lack of data.
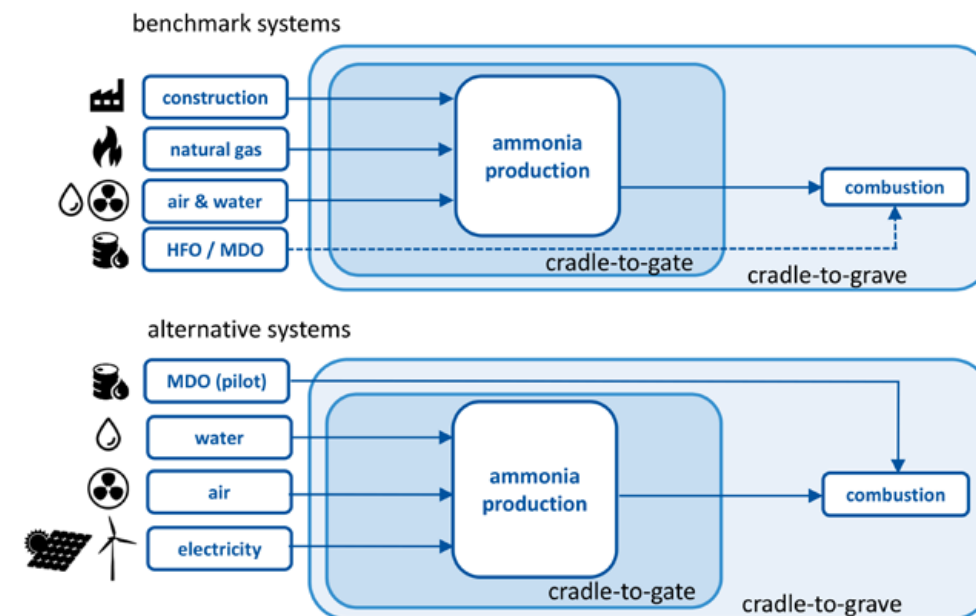

Figure 14: The system boundaries of the benchmark system include conventional ammonia production (cradle-to-gate) and heavy fuel oil (HFO)/ marine fuel oil (MDO); cradle-to-grave). The alternative product system comprises the alternative ammonia production (cradle-to-gate) and the subsequent utilization as a marine fuel (cradle-to-grave). Marine diesel oil (MDO) is also used as pilot.

In the life-cycle inventory (LCI) phase, all material and energy input and output flows of a product system throughout its life cycle are collected. In the following, we present the LCI for our study.

Ammonia production
In this section, we discuss the LCI data for ammonia production. Ammonia can be classified as brown ammonia, blue ammonia, or green ammonia, according to the production routes:

Brown ammonia is synthesized from hydrogen (H_2) based on fossil carbon sources such as methane, naphtha, heavy oil, and coal, plus nitrogen (conventional ammonia production route). Currently, ammonia is mainly synthesized via hydrogen from steam methane reforming (SMR) [39]. On average, fossil-based ammonia synthesis emits about 2.0 t CO_{2e}/t NH_3, accounting for 1.2 % of global anthropogenic CO_{2e} emissions [41]. Two-thirds of CO_{2e} is emitted during the reforming of hydrocarbons, while one-third occurs through fuel combustion in the synthesis (about 7.2-9.0 GJ/t NH_3). In the European Union, the total CO_2 equivalent emissions decreased from about 33.4 Mt of CO_2 in 1990 to 23.9 Mt of CO_2 in 2016 [41].
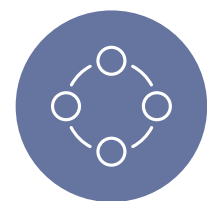
Blue ammonia is ammonia produced by the brown ammonia route combined with carbon capture and storage (CCS) for hydrogen production processes. Thus, the carbon footprint of blue ammonia is lower compared to brown ammonia due the avoided CO_2 emissions at the hydrogen production process. Electrification of heating processes as part of methane steam reforming (eSMR) can further reduce the carbon footprint of blue ammonia. Hydrogen can also be obtained as a by-product of other processes, resulting in a lower carbon footprint for ammonia synthesis. Ethylene crackers, chlorine plants, carbon black plants, and plastic gasification plants are examples of sources of by-product hydrogen with a lower carbon footprint [41].

Green ammonia can be produced in several ways: a) conventional ammonia synthesis cycle combined with electrolysis-based hydrogen, b) non-conventional technologies for ammonia synthesis, e.g., electrochemical synthesis, c) biomass-based hydrogen production with carbon capture and storage. In the 1950s and after, before cheap natural gas was available, electrolysis-based ammonia synthesis using hydropower was one of the most used technologies besides coal gasification [41]. Biomass-based hydrogen production with CCS can be an interesting option for small-scale green ammonia synthesis [41].

Blue ammonia and green ammonia from bio-based feedstocks
is out of the scope of this work.

Conventional Haber-Bosch process (brown ammonia)

Currently, more than 90 % of ammonia is globally produced by the Haber-Bosch process [42] and has, therefore, a Technology Readiness Level (TRL) of 9 [40]. This process is based on the following reaction:

$$N_2 + 3\,H_2 \leftrightarrow 2\,NH_3 \ (5)$$
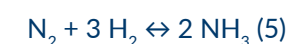
Typically, the reaction conditions are at temperatures of 400-500 °C and pressures of 200-300 bar. The most commonly used catalyst is Magnetite (Fe_3O_4) [43]. Today, approximately 50 % of ammonia production is based on hydrogen from steam methane reforming (SMR) [40]. Both production steps of the ammonia synthesis, steam methane reforming, and the Haber-Bosch processes are highly integrated processes (Figure 15).
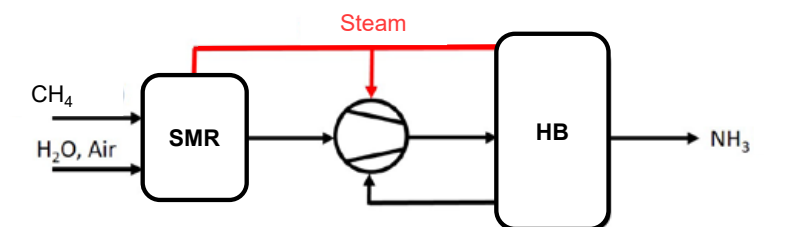

Figure 15: Simplified flowsheet of the conventional Haber-Bosch (HB) process with hydrogen from methanenatural gas (CH4) via steam methane reforming (SMR).

Electrified Haber-Bosch process (green ammonia)

Compared to the conventional Haber-Bosch process, the electrified Haber-Bosch process enables the integration of renewable electricity, replacing methane as both feedstock and fuel (Figure 16). Hydrogen is produced by water electrolysis. Here, we assume a PEM electrolyzer. Subsequently, hydrogen is converted to ammonia via the Haber–Bosch process, similar to the conventional process described before. Nitrogen can be provided

through cryogenic distillation (suitable for large-scale applications, e.g., marine fuel production) [40]. However, the electrified Haber-Bosch synthesis has an increased energy demand, and no internal waste heat SMR can be used [40]. The Haber-Bosch process is exothermic and generates heat (2.7 MJ per kgNH3) but no possible heat integration within the process [40]. This work considers no further utilization option for the generated heat representing a worst-case assumption. Depending on the applied electrolysis, the TRL of the electrified Haber-Bosch synthesis ranges from 6 to 9 [40].
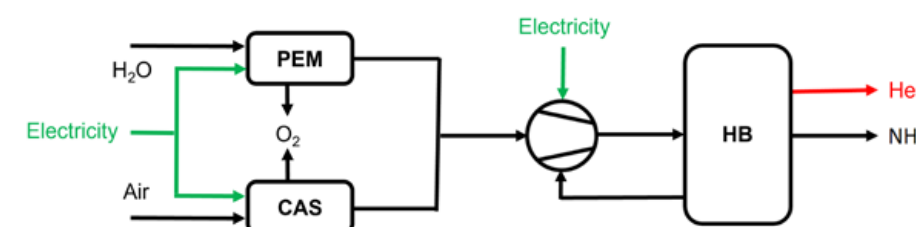

Figure 16: Simplified flowsheet of the electrified Haber-Bosch (HB) synthesis with hydrogen via PEM electrolysis and nitrogen from cryogenic air separation (CAS).

Electrochemical process (green ammonia)

Direct nitrogen electrolysis or electrochemical nitrogen reduction to ammonia is usually carried out under ambient conditions using nitrogen and water as feedstocks, thus an attractive alternative for ammonia production. In the nitrogen electrolyzer, nitrogen is fed into the cathode chamber and is reduced to ammonia, while water is oxidized to oxygen on the anode side (Figure 17) [44]. Compared to the conventional and the electrified Haber-Bosch synthesis, the electrochemical synthesis is a novel technology with a TRL between 1-3 [40]. Currently, selectivity and throughputs are low, which increases the energy demand far beyond the conventional Haber-Bosch process. However, future development could reduce the energy consumption of electrochemical synthesis [41]. Furthermore, the process concept is simple, and thus, could reduce the complexity through a more compact design [41, 45] compared to the conventional Haber-Bosch process.
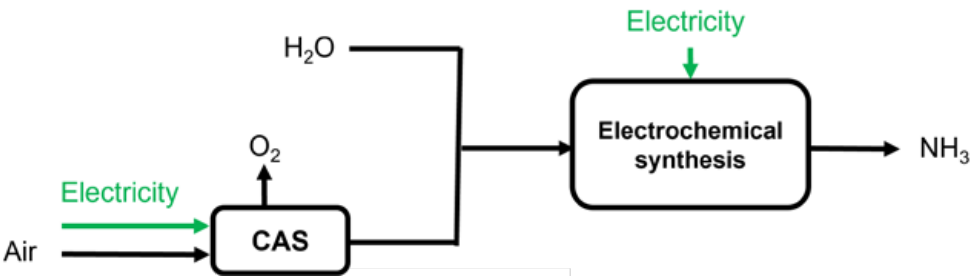

Figure 17: Simplified flowsheet of the electrochemical ammonia synthesis and nitrogen from cryogenic air separation. Electricity demands correspond to the today scenario (cf. Table 2)

Table 2 shows the electricity requirements for the considered ammonia processes, hydrogen production via a PEM electrolyzer, and nitrogen production via cryogenic air separation. For electrochemical synthesis and PEM electrolysis, we consider a today and a future scenario, as both technologies are currently under development and could have, therefore, a potential for improvements. The electrified Haber-Bosch process and cryogenic air separation are at an industrial TRL (8-9); thus, we consider only the today scenario without improvements for the future.

| Process | Electricity demand | | |
	Today	Future	Unit
Electrochemical synthesis	37.5	7.78	$kWh_{el}/kg\ NH_3$
Electrified Haber-Bosch synthesis [40],[46]	0.62 (0.48-0.75)		$kWh_{el}/kg\ NH_3$
PEM electrolysis [47]	49.7	41.6	$kWh_{el}/kg\ H_2$
Cryogenic air separation (nitrogen production) [46]	0.65 (0.5-0.8)		$kWh_{el}/kg\ H_2$

Table 2: Electricity demands for the electrochemical synthesis, electrified Haber-Bosch synthesis, PEM-electrolysis and cryogenic air separation.

For electricity supply, we consider the current electricity from wind power and photovoltaic power in the European Union as the lower bound for the carbon footprint of electricity supply (see Table 3). In addition, various country-specific grid mixes are considered in a sensitivity analysis.

Process	Database
EU-28: Electricity from photovoltaic	GaBi
EU-28: Electricity from wind power	GaBi
NO: Electricity grid mix	GaBi
FR: Electricity grid mix	GaBi
DK: Electricity grid mix	GaBi
GB: Electricity grid mix	GaBi
EU-28: Electricity grid mix	GaBi
ES: Electricity grid mix	GaBi
IT: Electricity grid mix	GaBi
DE: Electricity grid mix	GaBi

Table 3: Life-cycle inventory processes for the electricity supply [48].

We use ammonia from the conventional Haber-Bosch process and hydrogen via steam methane reforming for the cradle-to-gate system boundaries. For the cradle-to-grave system boundaries, diesel is used as pilot (cf. Section 4.2) and benchmark. Since marine ships often drive with heavy fuel oil (HFO), we consider HFO as the second benchmark.

Process	Database
EU-28: Ammonia (NH_3) Fertilizers	GaBi
EU-28: Diesel mix at refinery	GaBi
EU-28: Heavy fuel oil at refinery (2.5wt.% S)	GaBi

Table 4: Life-cycle inventory processes for the fossil-based benchmarks and pilot [48].

The life-cycle inventory data for the use phase can be found in Section 3.2 (Figure 9; realistic scenario).

5.3 CARBON FOOTPRINT ANALYSIS

Based on the life-cycle inventory data collected in Section 3, the life-cycle impact assessment (LCIA) can be conducted, and results can be interpreted. Life-cycle impact assessment translates all flows entering or leaving the life cycles to their effects on the considered environmental impact categories. In the following, we discuss the environmental assessment results along the ammonia life cycle.

5.3.1 CARBON FOOTPRINT OF AMMONIA PRODUCTION

For the today scenario, the carbon footprint of electrochemical and the electrified Haber-Bosch synthesis is reduced by 3 % and 75 % compared to the conventional Haber-Bosch synthesis (2.3 kg CO_{2e}/kg NH_3) when electricity from photovoltaics is used (Figure 18). Using the wind power, the carbon footprint is reduced by 85 % and 96 % for the electrochemical and the electrified Haber-Bosch processes, respectively.

The electrochemical process is more sensitive to the carbon footprint of the electricity due to its high electricity demand (37.5 kWh/kg NH_3; cf. Table 2), where nitrogen production accounts only for 1 % of the ammonia carbon footprint from the electrochemical process. For the electrified Haber-Bosch process, the largest contribution to carbon footprint occurs from the hydrogen production via the PEM-electrolyzer (approximately 90 %).
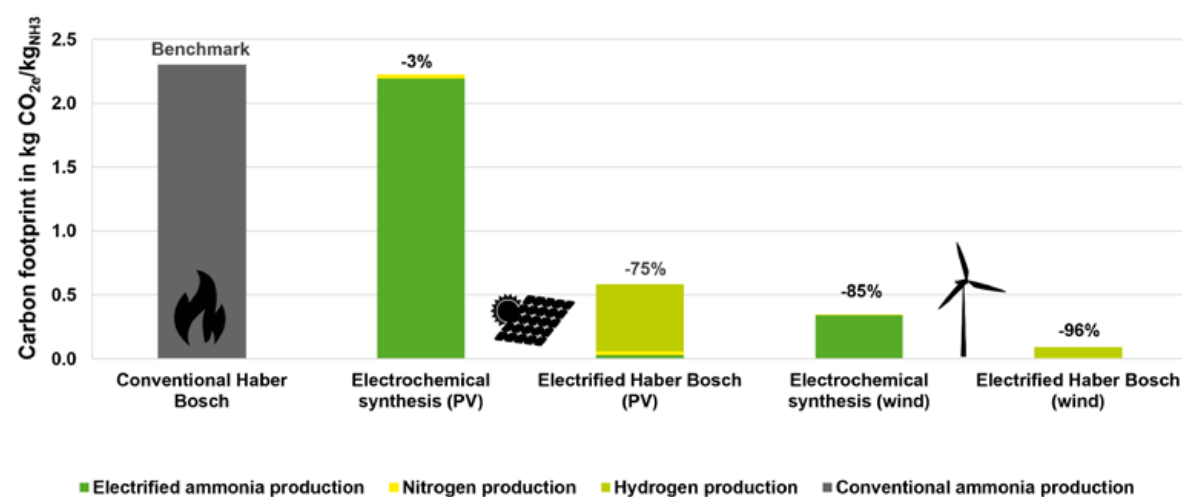

Figure 18: Carbon footprint of the considered ammonia production routes: conventional Haber-Bosch process and alternative production including electrochemical process and electrified Haber-Bosch process. Electricity is supplied by photovoltaics (PV) or wind.

The future scenario leads to improvements for the PEM electrolysis (cf. Table 2), resulting in a slightly lower carbon footprint of the electrified Haber-Bosch process using wind power (97%) compared to the today scenario (Figure 19). Potential improvements of electrochemical synthesis are expected to be higher than for the PEM electrolysis (cf. Table 2). In the future scenario, the carbon footprint of ammonia from the electrochemical process could be decreased to the one from the electrified Haber Bosch process while both using wind electricity.
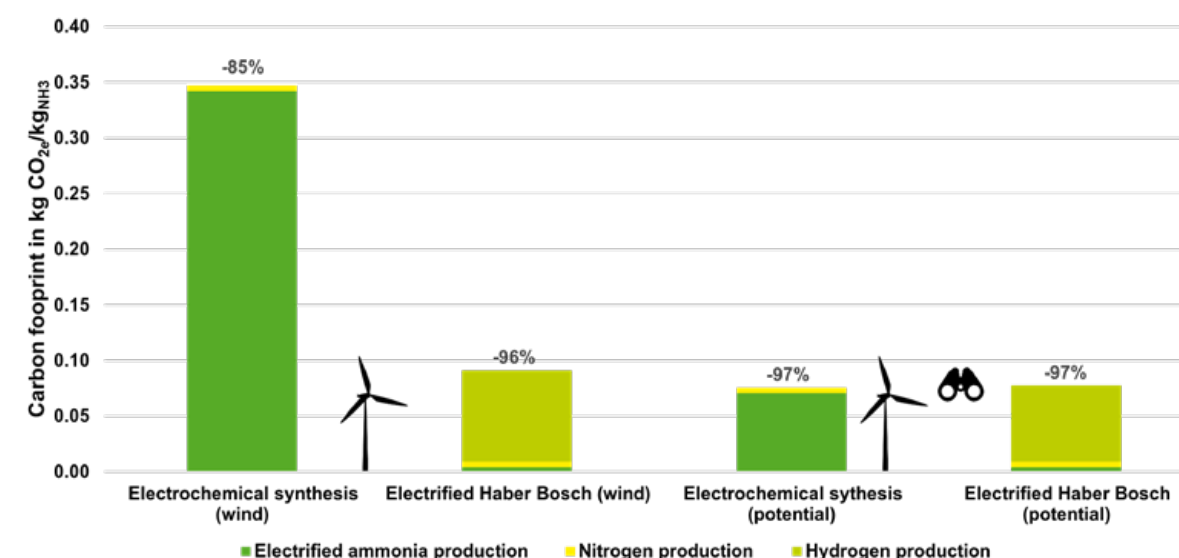

Figure 19: Carbon footprint of electrochemical synthesis and electrified Haber-Bosch using wind power for the today and the future scenario (potential).

The electricity supply for alternative ammonia processes represents the most crucial factor. So far, we solely illustrate the LCA results for wind and photovoltaic power, i.e., a best-case for the carbon footprint. Thus, we expand our study and vary the carbon footprint of the electricity supply in Figure 20. The carbon footprint of the alternative ammonia processes depends linearly on the carbon footprint of the electricity supply. This effect is stronger for the electrochemical process due to its high electricity demand. The black line represents the carbon footprint of conventional ammonia production. The crossing points of the green lines with the black line represent the break-even points. The break-even points specify the maximum carbon footprint for the electricity supply in which the alternative ammonia production is still beneficial compared to the conventional one. For the electrochemical process and the electrified Haber-Bosch process in the today scenario, the carbon footprint of the electricity supply needs to be lower than 60 and 231 g CO_{2e}/kWh$_{el}$, respectively. In the future scenario, the break-even points are reached at higher carbon footprints due to the potential technology improvements, and thus, lie between 270 and 276 g CO_{2e}/kWh$_{el}$. Figure 20 shows that synthetic ammonia production could reduce the carbon footprint of ammonia even today in countries such as Norway using the electrochemical process, or France using the electrified Haber-Bosch process.
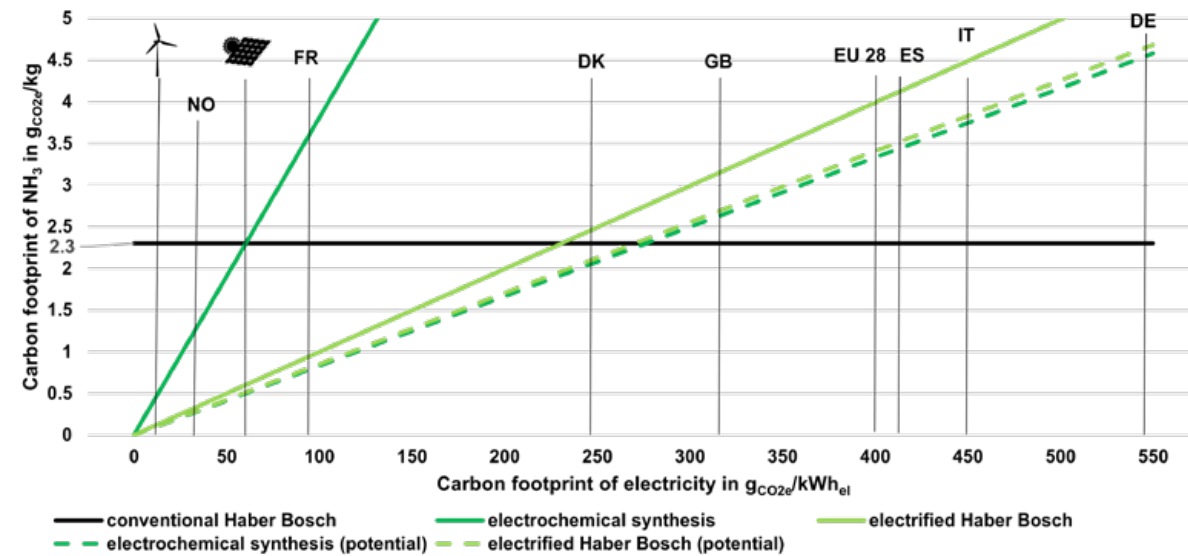
Figure 20: Carbon footprint of the considered ammonia production pathways: conventional Haber-Bosch process and alternative productions including electrochemical synthesis and electrified Haber-Bosch (y-axis) over the carbon foot footprint of the electricity supply.

Today the global ammonia production is about 150 Mt per year [40]. A transition of the conventional ammonia production to the electrified Haber-Bosch process (potential) could provide a greenhouse gas reduction potential of about 334 Mt CO_{2e}, when electricity is supplied by wind power.

However, this transition requires an additional electricity demand of 1280 TWh per year, corresponding to about 5 % of the global electricity consumption in 2018 [49]. Thus, a transition to synthetic ammonia would require a massive expansion of the electricity sector.

5.3.2 CARBON FOOTPRINT FOR AMMONIA AS MARINE FUEL

Here, we assess the carbon footprint of marine transportation utilizing ammonia from conventional or alternative production processes. Compared to heavy fuel oil, utilizing ammonia from the electrified Haber-Bosch process reduces the carbon footprint of marine transportation by 58 and 86 % for photovoltaic and wind power, respectively (Figure 21). Ammonia from the conventional Haber-Bosch process and electrochemical process powered by photovoltaics increase the carbon footprint of marine transportation by 40 and 36 % compared to heavy fuel oil, respectively. By using wind power, the electrochemical synthesis could reduce the carbon footprint of marine transportation by 71 % compared to heavy fuel oil.

Analog to Section 5.3.1, also here the high electricity demand of electrochemical process (37.5 kWh/kg NH3; cf. Table 2) is more sensitive to the carbon footprint of the electricity. For the considered alternative ammonia processes, the contribution of the pilot (fossil diesel) accounts for 1-5 %, the nitrogen supply for 1-4 %, and the combustion for 20-59 % of the carbon footprint, respectively. Considering the electrochemical process, ammonia production contributes 67-92 % to the carbon footprint of marine transportation. For the electrified Haber-Bosch process, ammonia production accounts for 2-4 % of the carbon footprint, whereby the largest contribution comes from the hydrogen production via the PEM-electrolyzer (32-67 %).

Figure 21: Carbon footprint of ammonia as marine fuel for considered production pathways: conventional Haber-Bosch process and alternative productions including electrochemical synthesis and electrified Haber-Bosch in the today scenario compared to heavy fuel oil. Electricity is supplied by photovoltaics (PV) and wind.

The future scenario considers improvements for the PEM electrolysis and the electrochemical processes (cf. Table 2), resulting in an equal carbon footprint for the marine fuels via both routes (97-98 g CO_{2e}/kWh_{mech}), i.e., 86% reduction compared to heavy fuel oil (Figure 22).
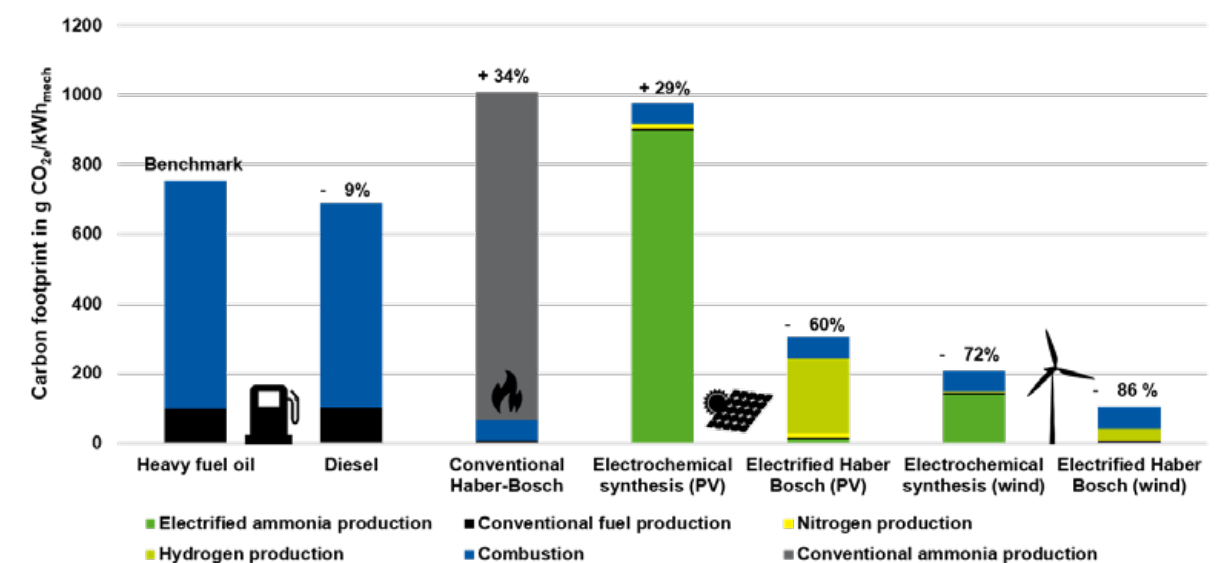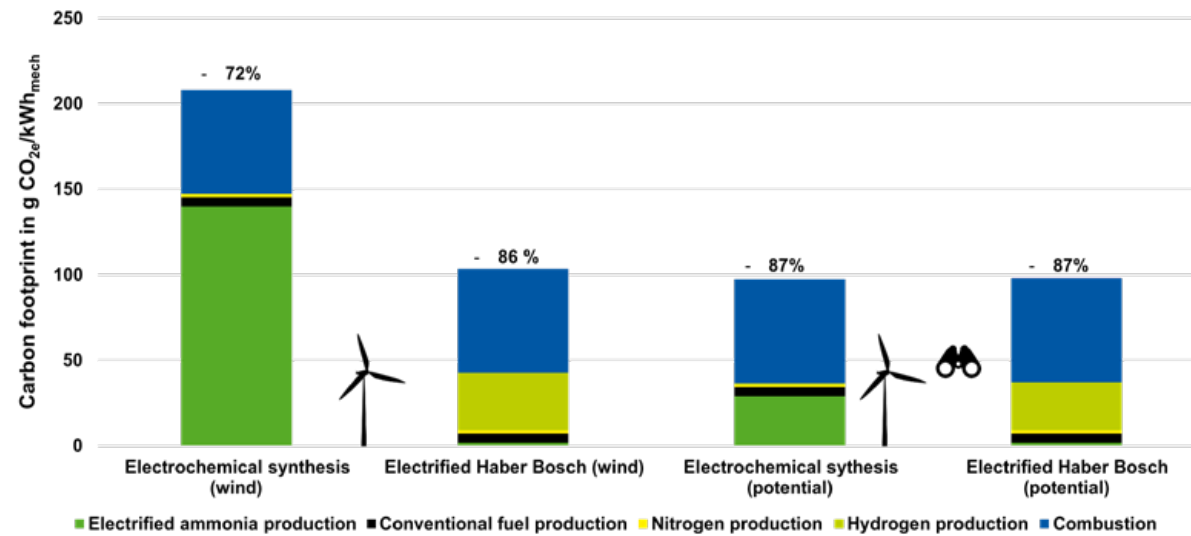

Figure 22: Carbon footprint of ammonia as marine fuel for considered production pathways: conventional Haber-Bosch process and alternative productions including electrochemical synthesis and electrified Haber-Bosch for the today and the future scenario. Electricity is supplied by wind.

The sensitivity study for the carbon footprint of ammonia as marine fuel in Figure 23 shows a linear dependence on the carbon footprint of the electricity supply. To reduce the carbon footprint of marine fuel compared to heavy fuel oil in the today scenario, the carbon footprint of the electricity supply has to be lower than 48 and 184 g CO_{2e}/kWh_{el} for the electrochemical process and the electrified Haber-Bosch process, respectively.

Due to the improved efficiencies in the future scenario, the carbon footprints of the electricity supply can be less clean (220 und 215 g CO_{2e}/kWh_{el}) than those for the today scenario. However, it is crucial to use an electricity mix with sufficiently large shares of renewable energy to reduce the carbon footprint with ammonia as marine fuel.
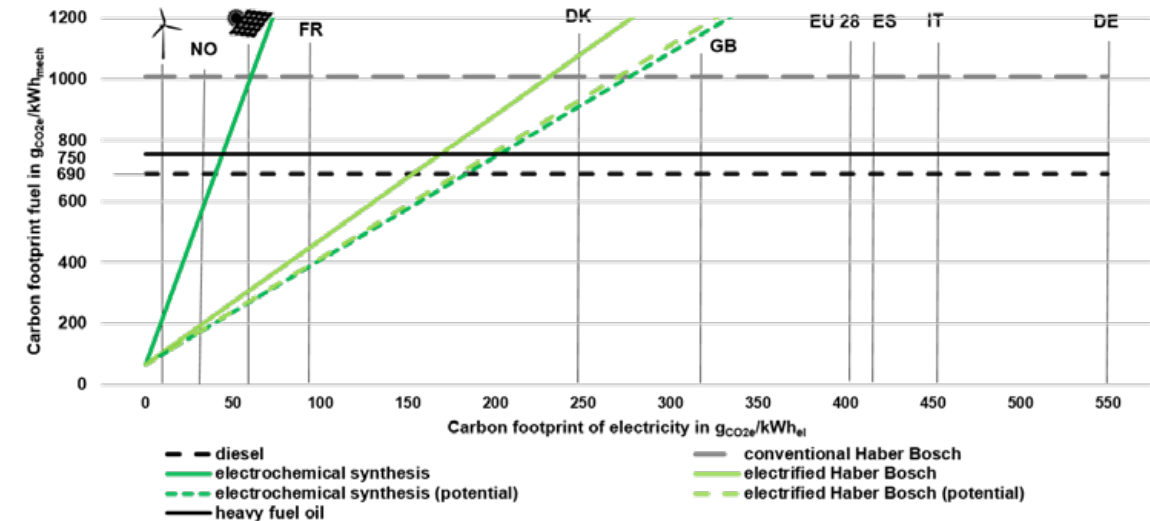

Figure 23: Carbon footprint of ammonia as marine fuel (y-axis) for the considered ammonia production pathways: conventional Haber-Bosch process and alternative productions including electrochemical synthesis and electrified Haber-Bosch over the carbon foot footprint of the electricity supply (x-axis).

Today, the share of shipping in the global oil demand is 5% [49, 50], corresponding to a global marine fuel demand of approximately 276 MtHFO (assumed as HFO). Using ammonia via the electrified Haber Bosch synthesis powered by wind as an alternative marine fuel offers a potential GHG emission reduction of 700 $MtCO_{2e}$ per year. However, the transition to ammonia as alternative marine fuel would lead to an additional electricity demand of 3710 TWh per year, corresponding to about 14 % of the global electricity consumption in 2018 [49].

A massive expansion of the electricity sector would be required to provide the additional input for using ammonia as synthetic marine fuel.

Our analysis shows the potential for GHG emission reductions of synthetic ammonia as marine fuel when powered with low-carbon electricity. However, other environmental impact categories need to be considered based on detailed production and engine-related emission data.

5.4 COST ANALYSIS

Figure 24 shows the fuel costs depending on the hydrogen price. The fossil marine fuel price varies between 34 and 62 €-ct. per litre$_{marine\ fuel\ eq.}$ [51]. We further added additional projected social costs of carbon up to 118 €-ct. per litre$_{marine\ fuel\ eq.}$. For hydrogen production via a PEM electrolyzer, the hydrogen price varies between 2.00 - 3.87 and 2.64

- 5.56 € per kgH_2 for 2050 and today, respectively, when powered by wind and PV from the MENA states or wind from the Baltic sea [52], respectively. For synthetic ammonia production, we consider the electrified Haber Bosch synthesis in the cost analysis since this route has a high TRL (cf. Section 5.2).

For the cost analysis of synthetic ammonia production, we assume simplifying the OPEX for hydrogen production since the electricity demand for the PEM electrolyzer accounts for 97 % of the total synthesis electricity demand. Synthetic ammonia production depends strongly on the hydrogen price (Figure 24). The break-even points are shown by crossing the red ammonia line with the fossil marine fuel area. The hydrogen price need to be lower than 2 € per kg_{H2} for which synthetic ammonia would be cost-competitive to fossil marine fuel. Not even synthetic ammonia produced from hydrogen via wind and PV power in the MENA states 2050 would be cost-competitive to fossil marine fuel. However, projected social carbon costs increase the fossil marine fuel price by up to further 118 €-ct. per $litre_{marine\ fuel\ eq.}$. Considering the social carbon costs, synthetic ammonia has the potential to be cost-competitive to fossil marine fuel for a broader range of hydrogen supply scenarios (today MENA, 2050 MENA, and 2050 Baltic sea). However, our cost analysis is solely based on the OPEX for the hydrogen supply and needs to be refined for a more in-depth analysis, including CAPEX and other OPEX.
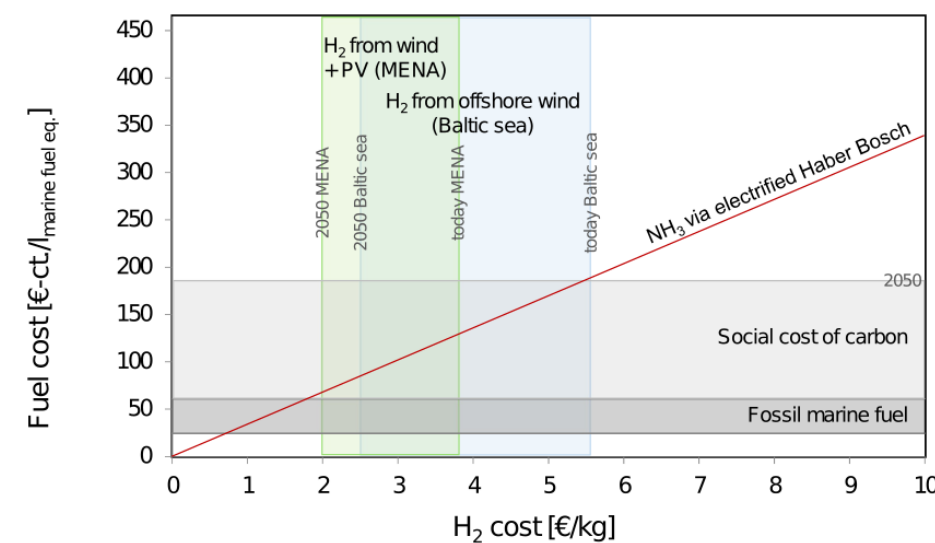
As Ammonia has a low energy content it will always require larger tanks for storage. Therefore, a vessel designed for using ammonia as primary fuel compared to a vessel using conventional fuels will always either be larger or have a decreased cargo capacity. Alternatively, this vessel would have a reduced endurance and need more frequent bunkering.

Considering the special needs of alternative fuels and Ammonia in particular, there has to be a holistic approach in optimizing the vessel design, entirely. Being Ammonia-"Ready", will most likely be a wrong compromise. The vessel design, starting with tank arrangement, special dedicated exhaust gas aftertreatment equipment, safety areas, the use of specific material, need to be reconsidered. Within a next step it is recommend to define a design base with an interested ship owner and to work on a new concept design for an optimized F-Type, the "F-Ammonia".

The LCA results show that synthetic ammonia has the potential to reduce the carbon footprint compared to conventional ammonia and as an alternative marine fuel. These potential reductions are achieved when using low-carbon electricity. Suitable electricity sources are based on renewable energies and grid mixes with a large share of renewable or nuclear electricity. Today, sufficient clean electricity is available, for example, in Norway, France, and Denmark. Synthetic ammonia enables the integration of renewable energy into the chemical (e.g., fertilizer) and transportation sectors. However, an increase of the electricity sector is required to provide the additional input for synthetic ammonia production. Considering the simplified cost analysis, costs for synthetic ammonia depend strongly on the hydrogen price. Synthetic ammonia can only be competitive when cheap hydrogen can be used, or if social carbon costs are added to the conventional marine fuel. However, to avoid burden shifting, further research is required to evaluate other environmental impacts beyond the carbon footprint of ammonia as marine fuel based on detailed production and engine-related emission data. Furthermore, a refinement of the rough cost estimate is needed to consider both infrastructure and transport cost.

Based on the results of Part B to D, the authors are confident that a solid base for a continuation is set. Working in close cooperation with researcher, operator, classification societies and suppliers would be beneficial in developing a respective concept design and a pressing need is unavoidable in lieu of the climate change and to reduce the carbon footprint.

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