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Sources, technologies and life cycle assessment of ammonia production

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ABSTRACT:

Ammonia is the most basic feedstock in fertilizer production. At the same time, it is aimed to be used in future internal combustion engines to reduce the use of fossil fuels. Many trials have been carried out in testing ammonia in engines and it is found to be a promising alternative fuel especially in marine industry. In addition, it is also frequently used in the textile industry.

Ammonia has many different methods for production. Natural gas is the most important source to produce ammonia globally but in order to reduce the environmental impact of the production, green ammonia production methods are required. Life Cycle Assessment (LCA) is an important tool for examining potential environmental impacts from ammonia production.

The aim of this study was to examine the environmental impact of four different production methods of ammonia. They were blue, grey, green (via electrolysis) and green (biomass based) ammonia. The method for evaluating the impact of the production methods was LCA calculations which was conducted in line with the International Maritime Organization (IMO) LCA guidelines. The greenhouse gas (GHG) mission values that may occur in ammonia production were calculated.

The calculations show that the lowest GHG emissions from ammonia production are obtained from green ammonia produced from renewable hydrogen via electrolysis, and the second lowest emissions come from green ammonia produced from biomass. The highest GHG emissions are formed in grey ammonia production and the second highest from blue ammonia production. Based on the findings of this thesis, it is clear that there is a huge need to reduce the use of fossil fuels in ammonia production. The use of sustainable biomasses and renewable energy-powered electrolysis-based hydrogen in ammonia production can significantly reduce the climate impacts of ammonia production.

KEYWORDS: ammonia, GHG emissions, LCA calculations, carbon content, ammonia production

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TIIVISTELMÄ:

Ammoniakki on lannoitetuotannon perus raaka-aine. Vihreää ammoniakkia halutaan käyttää tulevissa polttomoottoreissa fossiilisten polttoaineiden sijaan. Monia kokeita ammoniakin moottorikäytöstä on tehty, ja tulosten perusteella ammoniakki on lupaava vaihtoehtoinen polttoaine erityisesti merenkulkuun. Sitä käytetään usein myös tekstiiliteollisuudessa. Ammoniakilla on useita erilaisia tuotantomenetelmiä. Maakaasu on tärkein raaka-aine maailmanlaajuisessa ammoniakin tuotannossa, mutta tuotannon ympäristövaikutusten vähentämiseksi tarvitaan vihreän ammoniakin tuotantomenetelmiä. Elinkaariarviointi (Life Cycle Assessment, LCA) on tärkeä väline ammoniakin tuotannon mahdollisten ympäristövaikutusten tutkimiseen.

Diplomityön tavoitteena oli tutkia ammoniakin neljän erilaisen tuotantomenetelmän ympäristövaikutuksia. Valitut tuotantomenetelmät olivat sinisen, harmaan, ja kahden eri tavalla valmistetun vihreän (elektrolyysin kautta sekä biomassasta valmistetun) ammoniakin tuotantotavat. Ympäristövaikutusten arviointimenetelmänä käytettiin elinkaarilaskelmia, jotka noudattivat IMO:n (International Maritime Organization) ohjeistusta. Ammoniakin tuotannossa mahdollisesti esiintyvien kasvihuonekaasujen pitoisuudet laskettiin.

Laskelmat osoittivat, että pienimmät kasvihuonekaasupäästöt saatiin uusiutuvasta vedystä elektrolyysin avulla tuotetusta vihreästä ammoniakista ja toiseksi pienimmät päästöt biomassasta tuotetusta vihreästä ammoniakista. Suurimmat kasvihuonekaasupäästöt syntyivät harmaan ammoniakin tuotannossa ja toiseksi suurimmat sinisen ammoniakin tuotannossa. Tulosten perusteella on selvää, että fossiilisten polttoaineiden käytön vähentämiselle ammoniakin tuotannossa on valtava tarve. Kestävien biomassojen ja uusiutuvalla energialla toimivan elektrolyysipohjaisen vedyn käytöllä ammoniakin tuotannossa voidaan vähentää merkittävästi ammoniakin tuotannon ilmastovaikutuksia.

AVAINSANAT: ammoniakki, kasvihuonekaasupäästöt, elinkaarilaskenta, hiilipitoisuus, ammoniakin tuotanto

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Abbreviations

AIN	Aluminum nitride
AE	Auxiliary engine
AE	Alkaline electrolysis
AR6	Sixth assessment report
AWE	Alkaline water electrolysis
CCS	Capture and storage
LCA	Life cycle assessment
MEC	Microbial electrolysis cells
GHG	Greenhouse gases
WtW	Well-to-tank
TtW	Tank-to-wake
WtW	Well-to-wake
IMO	International maritime organization
IEA	International energy agency
LNG	Liquified natural gas
MDO	Marine diesel oil
LHV	Lower heating value
FICFB	Fast internal circulating fluidized bed

SMR	Steam methane reforming
ME	Maine engine
IPCC	Intergovernmental Panel on Climate Change
SCR	Selective catalytic reduction
EGR	Exhaust gas recirculation
PEM	Polymer electrolyte membrane electrolysis
SOE	Solid oxide electrolysis
MMBtu	Million British thermal units
SFC	Specific Fuel Consumption
GWP	Global warming potential
KBR	Kellogg Brown & Root

Other Symbols

C_f	Emission factor
P_{ME}	Power output of main engine
P_{AE}	Power output of auxiliary engine
SFC_{AE}	Specific Fuel Consumption - auxiliary engine
SFC_{ME}	Specific Fuel Consumption - main engine
CO_2	Carbon dioxide
CH_4	Methane
N_2O	Nitrous oxide
$C_{f\ MDO}$	MDO emission factor
$C_{f\ LNG}$	LNG emission factor
$C_{f\ N_2O}$	N_2O emission conversion factor
$C_{f\ CH_4}$	CH_4 emission conversion factor
GWP_{N_2O}	Global warming potential of N_2O
GWP_{CH_4}	Global warming potential of CH_4

1 Introduction

Ammonia (NH_3) serves as a versatile chemical utilized across a wide array of industries due to its multifaceted properties. Ammonia is the most basic feedstock in fertilizer production. At the same time, it is aimed to be used in future internal combustion engines to reduce the use of fossil fuels. Many trials have been carried out in testing ammonia in engines and it is found to be a promising alter-native fuel especially in marine industry. In addition, it is also frequently used in the textile industry.

There are many ammonia production pathways. Ammonia is primarily produced from fossil resources, such as hydrocarbons extracted from underground sources or oil wells. Natural gas is the most important source to produce ammonia in global ammonia production, and the product is then called grey ammonia. If the production of grey ammonia includes carbon capture, the product is called blue ammonia. One of the most important problems of today's world is the increase in carbon dioxide, CO_2, emissions in the world. The effects of the increase in the amount of emissions on the environment are felt and important decisions are taken to reduce emission. The Paris climate agreement has been signed to reduce CO_2 emissions in the atmospheres by the countries. Ammonia production from fossil fuels generates substantial greenhouse gas (GHG) emissions that must be mitigated. A solution to this is to develop and invest on sustainable, green ammonia production. Green ammonia can be produced either via electrolysis, producing first hydrogen and then ammonia, or from biomass.

Life cycle assessment, LCA, is an important way to evaluate sustainability of ammonia production, and the impact of the production on the environment. Life cycle assessment enables examination from both production and environmental perspectives. The objective of this thesis is to examine the environmental impact of four different production methods of ammonia. The selected production methods include gray and blue ammonia, as well as two types of green ammonia: one produced through electrolysis and the other via biomass gasification. The method for evaluating the impact of the production methods was LCA GHG calculations and the calculations were made in line with the International Maritime Organization (IMO) LCA guidelines.

In calculations, the entire process was considered, from ammonia production to its end use as fuel in the engine. The stages that were considered when performing a life cycle assessment are shown in Figure 1.

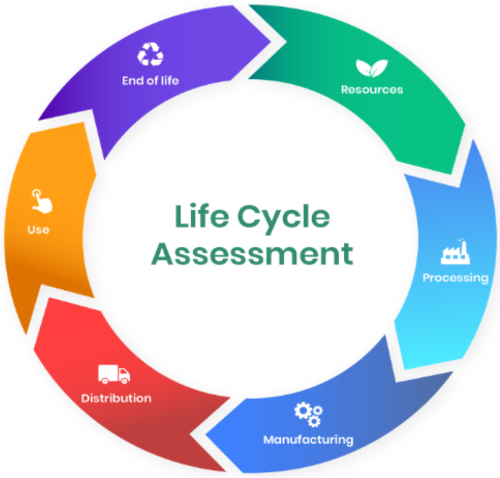


Figure 1. The Life-cycle assessment stages (Bieniek, 2023).

Production schemes of life cycle assessments were defined for each ammonia production method. The calculations included the raw material used in ammonia production, the transportation of the raw material to the production point, the production itself and the end use of the produced ammonia as engine fuel. The obtained results were used to compare the impact of each production method has for the environment.

2 Ammonia

Ammonia (NH_3) is a colorless gas with a strong odor, widely used in industries like agriculture and manufacturing. It is crucial in producing fertilizers and chemicals. Naturally, ammonia supports biological processes, helping synthesize amino acids and nucleotides, and plays a key role in the nitrogen cycle, aiding nutrient recycling in ecosystems. Inhaling ammonia can irritate and damage the respiratory system. High concentrations may cause severe burns, airway damage, and respiratory failure, while low levels can lead to coughing and throat irritation. Prolonged exposure may reduce sensitivity to its odor, increasing the risk of unnoticed harm (Taiyugas n.d).

Ammonia plays a significant role in global agricultural systems, particularly through its use in fertilizer production. As a key component in the production of all mineral nitrogen fertilizers, it converts atmospheric nitrogen into a form that can be used to support food supply. Around 70% of global ammonia production is directed towards fertilizer manufacturing, while the remaining amount is used in various industrial processes such as the production of plastics, explosives, and synthetic fibers. In recent years, ammonia has also been explored as a potential fuel source in the context of clean energy transitions. However, this application is still in its early stages and has not yet been widely adopted (IEA, 2021).

The benefits and usage activities of using clean resources in ammonia production are shown in Figure 2. The most feasible way to produce ammonia is to make it from renewable energy sources. Ammonia can be used as fuel in energy, in cleaning materials, and as a refrigerant in cooling systems (Dincer & Erdemir, 2020).

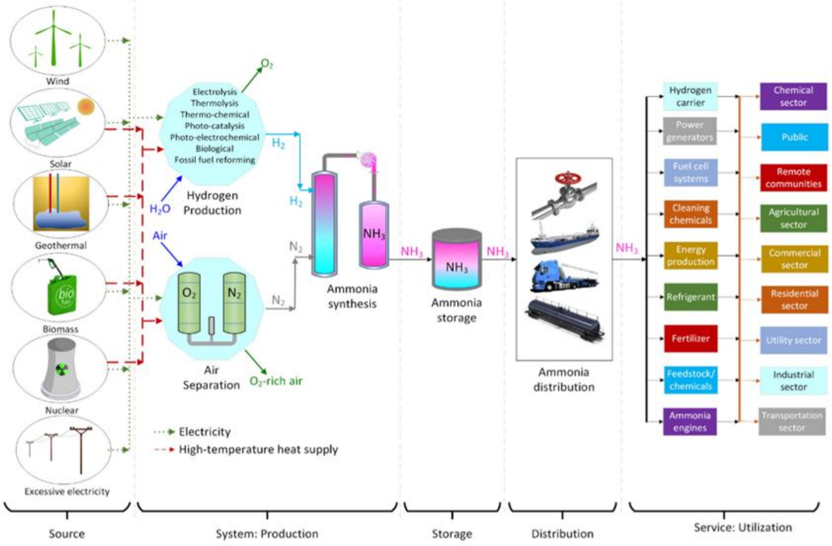
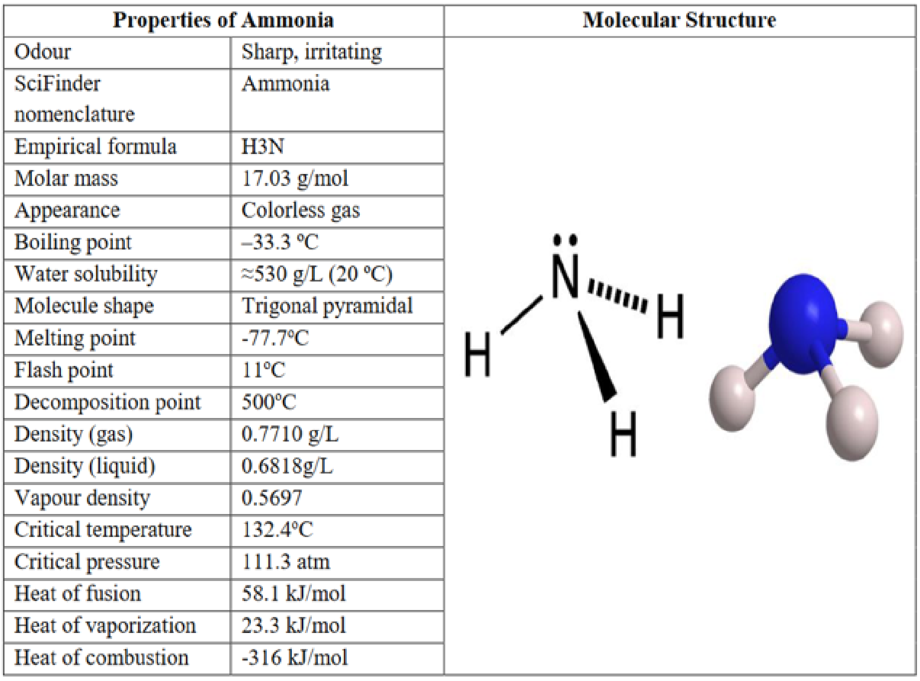


Figure 2. Sources, production stages and distribution for ammonia (Dincer & Erdemir, 2020).

Ammonia (NH_3) is synthesized using hydrogen and nitrogen as fundamental components. It exists as a gas under ambient conditions due to its boiling point of -33 °C and freezing point of -78 °C. With a critical temperature of 132.4 °C, ammonia transitions into a supercritical fluid at higher temperatures. Ammonia is highly soluble in water (~530 g/L at 20 °C) and features thermodynamic characteristics like a heat of vaporization of 23.3 kJ/mol. These properties make it suitable for applications in energy, agriculture, and refrigeration while requiring careful handling due to its flammability (Wilson et al., 2024). The properties of ammonia are shown in Figure 3.



Properties of Ammonia		Molecular Structure
Odour	Sharp, irritating	
SciFinder nomenclature	Ammonia	
Empirical formula	H3N	
Molar mass	17.03 g/mol	
Appearance	Colorless gas	
Boiling point	–33.3 °C	
Water solubility	≈530 g/L (20 °C)	
Molecule shape	Trigonal pyramidal	
Melting point	-77.7°C	
Flash point	11°C	
Decomposition point	500°C	
Density (gas)	0.7710 g/L	
Density (liquid)	0.6818g/L	
Vapour density	0.5697	
Critical temperature	132.4°C	
Critical pressure	111.3 atm	
Heat of fusion	58.1 kJ/mol	
Heat of vaporization	23.3 kJ/mol	
Heat of combustion	-316 kJ/mol	

Figure 3. The properties of ammonia (Wilson et al., 2024).

The first ammonia synthesis process was initiated by German chemist Fritz Haber and British chemist Robert Le Rossignol in 1909. Ammonia was obtained by distillation with compressed air. This technology was not suitable for ammonia production and was later developed further by Carl Bosch and his colleagues who were working at the German company BASF. The first ammonia plant was opened in 1913 at Oppau, Germany. Hydrogen production was achieved through a coal-based process (Lefferts et al., 2022).

183 million tons of ammonia is produced annually in the world from fossil feedstock, mostly from natural gas and coal. Ammonia can also be produced from renewable sources, which currently covers 0.01% of global ammonia production. Ammonia production has an impact on the environment, and the annual emission value of ammonia production is 0.5 Gt of CO_2. The emission value resulting from the production of ammonia is estimated to correspond to 1.0 % of CO_2 at the global level (Lefferts et al., 2022).

Renewable hydrogen production has a very important role for renewable ammonia production because ammonia production is actualized via electrolysis-based hydrogen. In history, hydropower has been an important renewable electricity source for alkaline electrolyzes for hydrogen production. The synthesis of renewable ammonia was developed and commercialized in 1921, and since the second half of the 20th century (1960s-2020s), the effects and development of renewable ammonia have been studied (Lefferts et al.,2022). The sources for ammonia production from 1915 to 2030 is shown in Figure 4. The Figure 4 also shows the increase of renewable ammonia production that is predicted to be seen from 2025 to 2030.

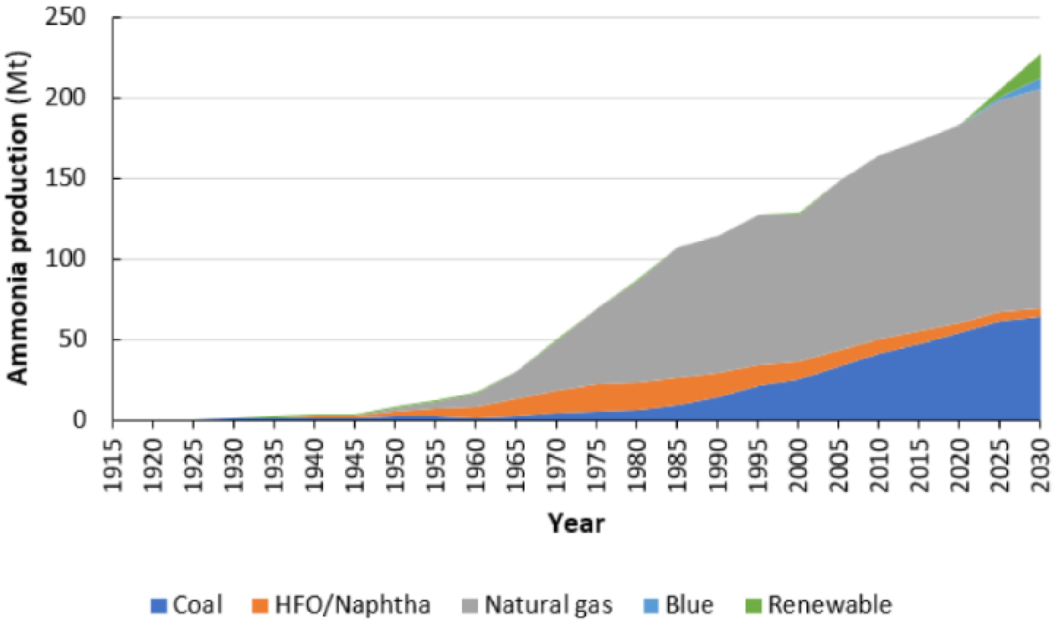


Figure 4. Sources used in ammonia production from 1915 to 2030 (Lefferts et al.,2022).

In 2019, China was the largest producer of ammonia, with a production of 53.5 million tons, representing 29% of global production. Additionally, China was the largest consumer of ammonia, with a consumption of 54.3 million tons. Following China, the leading ammonia producers included Russia (10%), the United States (9%), the Middle East (9%), the European Union (8%), and India (8%) (IEA, 2021). The data for the countries with the highest ammonia production and consumption in 2019 are presented in Figure 5.

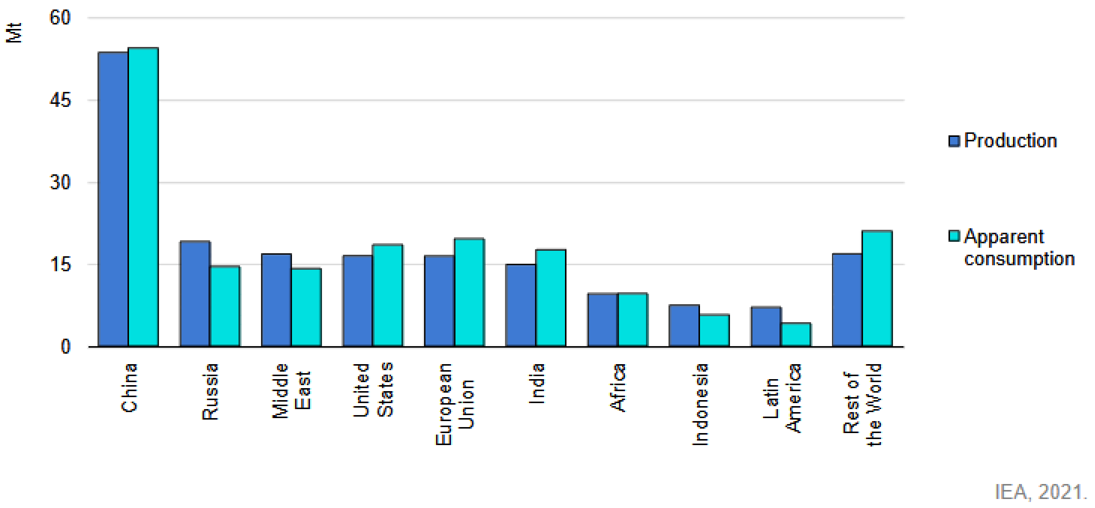


Figure 5. The largest producers and consumers of ammonia globally in 2019 (IEA, 2021).

3 Ammonia production

Ammonia production involves several key stages, including steam formation, water-gas shift reaction, CO_2 removal, synthesis gas purification, and ammonia synthesis and separation. The process requires a high level of energy and energy density. The total emissions from ammonia production are estimated at 289.8 Mt-CO_2, which represents approximately 0.93% of global CO_2 emissions. The energy consumption for ammonia production generally ranges from 28 to 37 GJ/t, which includes the energy needed to convert raw materials into ammonia throughout the entire production process (Aziz et al., 2020). The schematic diagram of the ammonia production using natural gas is shown in Figure 6.

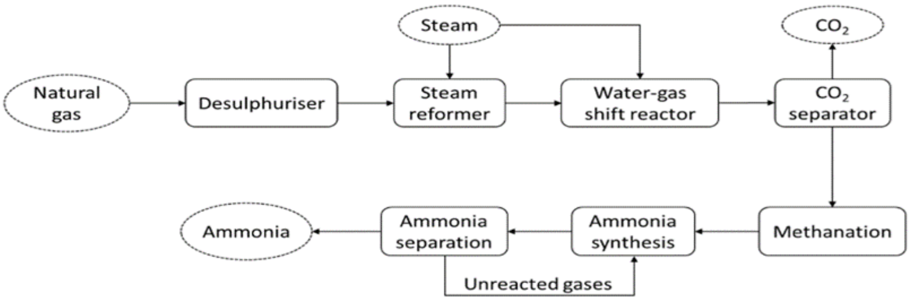


Figure 6. Schematic diagram of ammonia production using natural gas (Aziz et al., 2020).

3.1 Haber-Bosch method

The Haber Bosch is the most commonly used method to produce ammonia. Nitrogen obtained from the air is used directly to produce ammonia. In this method, ammonia production is carried out under high pressure and moderately high temperatures. The reaction is actualized using a catalyst generally made of iron. The lower the temperature and the higher the pressure used during ammonia production; the more ammonia is received. Production of ammonia is usually realized between 200 - 400 atm pressures and 400-650 °C temperatures (Encyclopaedia Britannica, 2024). One example of the schematic diagram of ammonia production via electrolysis including Haber-Bosch synthesis is shown in Figure 7.

$N_2 + 3 H_2 \rightarrow 2 NH_3$ (AH = -92,4 kJ · mol

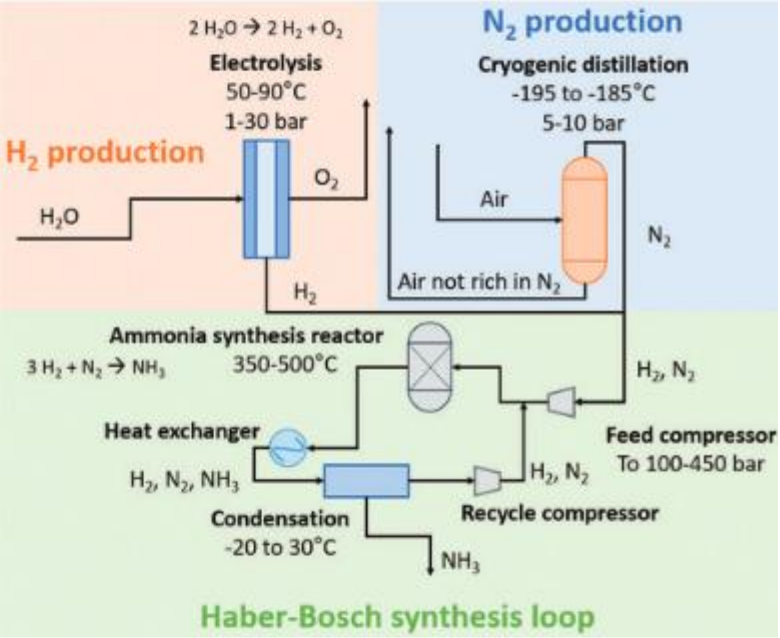


Figure 7. Schematic diagram of ammonia production (electrolysis-based) where Haber-Bosch synthesis is included (Jardali et al., 2021).

The industrial Haber-Bosch process involves the reaction of nitrogen and hydrogen gas in a pressure vessel containing a special catalyst to accelerate the reaction. When examined from a thermodynamic perspective, ammonia production can be achieved at room temperature and pressure, but the production is not at the required level. It is an exothermic reaction. With the effect of increasing temperature and pressure, the balance is in the direction of increasing production capacity. Ammonia production was initially carried out by electrolysis of water, but later natural gas was the main feedstock. The main reason for using natural gas is that it is hydrocarbon compound, methane gas. (Helmenstine, n.d). An example of the Haber Bosch method to produce ammonia is shown in Figure 8.

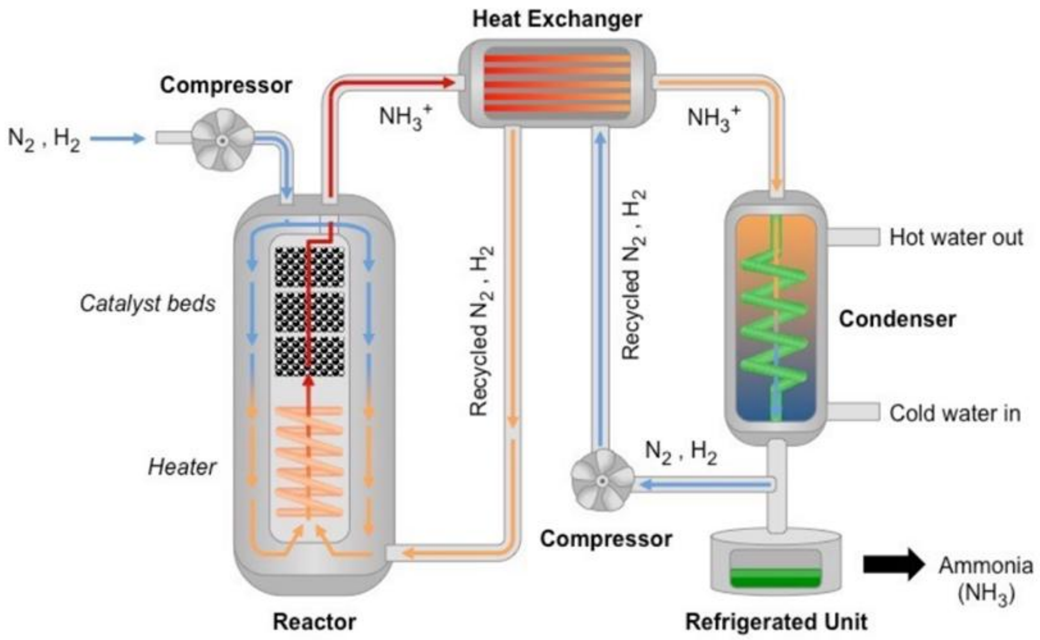


Figure 8. An example model of Haber Bosch method to produce ammonia (Wilson et al., 2024).

3.2 Other methods

In addition to Haber-Bosch, some other production processes exist and they are shortly introduced in this chapter.

Frank-Caro

The Frank-Caro process is developed by Nicodemus Caro and Adolphe Franck, and with this method a very simple transformation of cyanide via the reaction of calcium carbide and nitrogen ($CaC_2 + N_2 = CaCN_2 + C$) is made. Again, the intermediate product is converted into ammonia by water vapor reaction ($CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$). The Frank Caro process is the first commercial synthesis in the world at the global level (Xiang et al., 2023).

Thermal Catalytic

The synthesis of ammonia (NH_3) is thermodynamically promoted under conditions of high pressure and low temperature. Nevertheless, in terms of kinetics, temperatures above 200 °C are necessary to achieve substantial conversion rates. To reconcile these kinetic and thermodynamic requirements, the ammonia synthesis process is commonly carried out at moderate temperatures (400–450 °C) and elevated pressures (150–250 atm), which results in conversion efficiencies of 10–15% per cycle. The operating conditions associated with thermo-catalytic NH_3 synthesis present significant challenges, primarily due to the high energy consumption and the relatively poor stability of the catalysts used (Mateo et al., 2024).

Distillation Method

Before the first World War, ammonia production was primarily achieved through dry distillation of nitrogen-rich plant materials and animal by-products. This process typically involves the reduction of nitrous acid and nitrites with hydrogen. Additionally, ammonia was synthesized by distilling coal or by decomposing ammonia salts with alkaline hydroxides such as quicklime. For laboratory-scale synthesis, an alternative method included heating urea with calcium hydroxide, resulting in the formation of ammonia and calcium carbonate (Toppr, n.d.). The chemical reactions are represented as follows:

$2NH_4Cl+2CaO \rightarrow CaCl_2+Ca\ (OH)_2+2NH_3(g)$

$(NH_2)_2CO+Ca\ (OH)_2 \rightarrow CaCO_3+2NH_3$

Steam Distillation

Steam distillation technique is used for the distillation of heat-sensitive components. In this technique, the boiling point of the components is lowered by passing water vapor through the mixture to be distilled. Condensation occurs and titration techniques are used with the resulting water solution for analytical quantification. Steam distillation technique is generally used in the separation of aromatic components or oils of natural products and in the Kjeldahl nitrogen determining. Kjeldahl nitrogen determination is carried out in three basic steps, which include digestion, steam distillation and titration. (Buchi, n.d) These basic steps are shown in Figure 9.

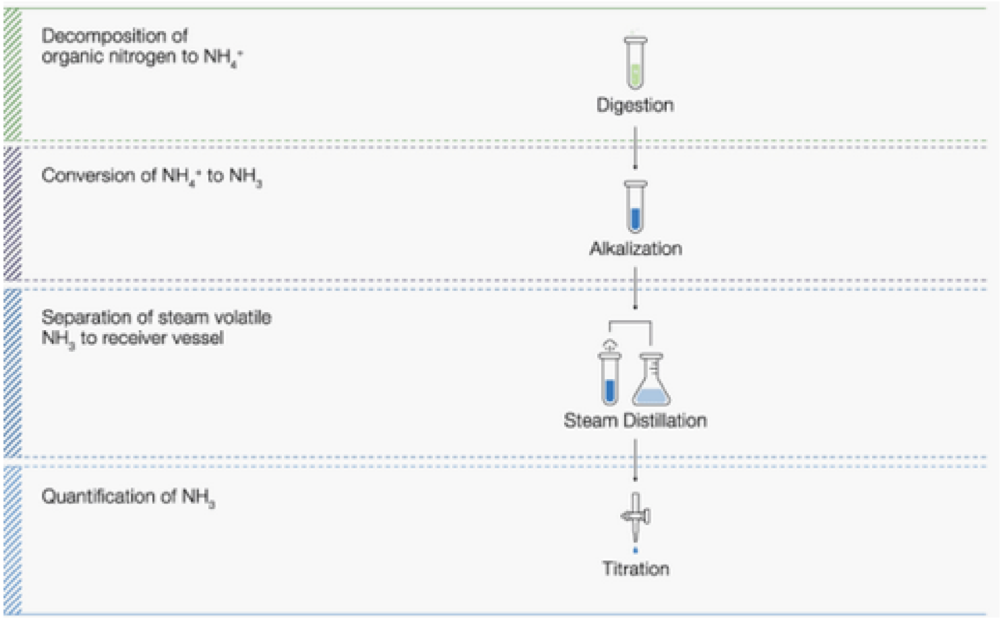


Figure 9. The stages in Kjeldahl nitrogen determinations (Buchi, n.d).

Realization of the thermochemical cycle in ammonia production

Primary energy sources need to be pretreated and converted to carbon before the thermochemical cycle process occurs. The aluminum nitride (AlN) production is performed via carbothermal reduction of AlO_3 and nitrogen, this production is actualized in the first reduction process. AlN production is carried out under a temperature of 1500 °C and this production is endothermic. In addition, steam hydrolysis is carried out in the second reaction, the AlN produced in the first reduction reacts with steam to produce Al_2O_3. Al_2O_3 is produced from the second reaction and then circulated to the first production reaction (Aziz et al., 2020.). The schematic diagram of this production is shown in Figure 10.

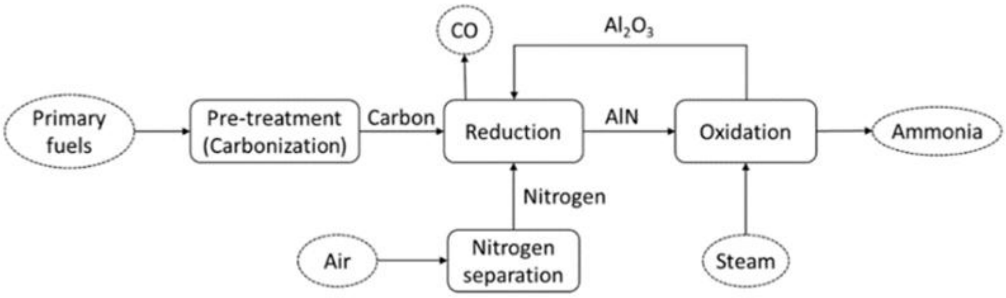


Figure 10. The created schematic diagram for ammonia production and thermochemical cycle. (Aziz et al., 2020).

3.3 Development of ammonia plants

The modern ammonia production plants were developed between 1950-1980. After 1980s the development work was continued on designing models for modern ammonia plants. The most important purpose of establishing modern ammonia plants was to reduce the use of fossil fuels and turn to renewable resources (Richardson & Pattabathula, 2016).

The first ammonia plant was established as a single converter ammonia plant by M.W. Kellog in the 1960s. The capacity of production was 544 metric tons daily. In this plant, a four-case centrifugal compressor was used and compression with synthesis gas up to 152 bar pressure was supported. The highest possible operation pressure was 324 bar. The process was carried out with a piston compressor. (Richardson & Pattabathula, 2016). Figure 11 shows a single concept ammonia plant designed by M.W. Kellog.

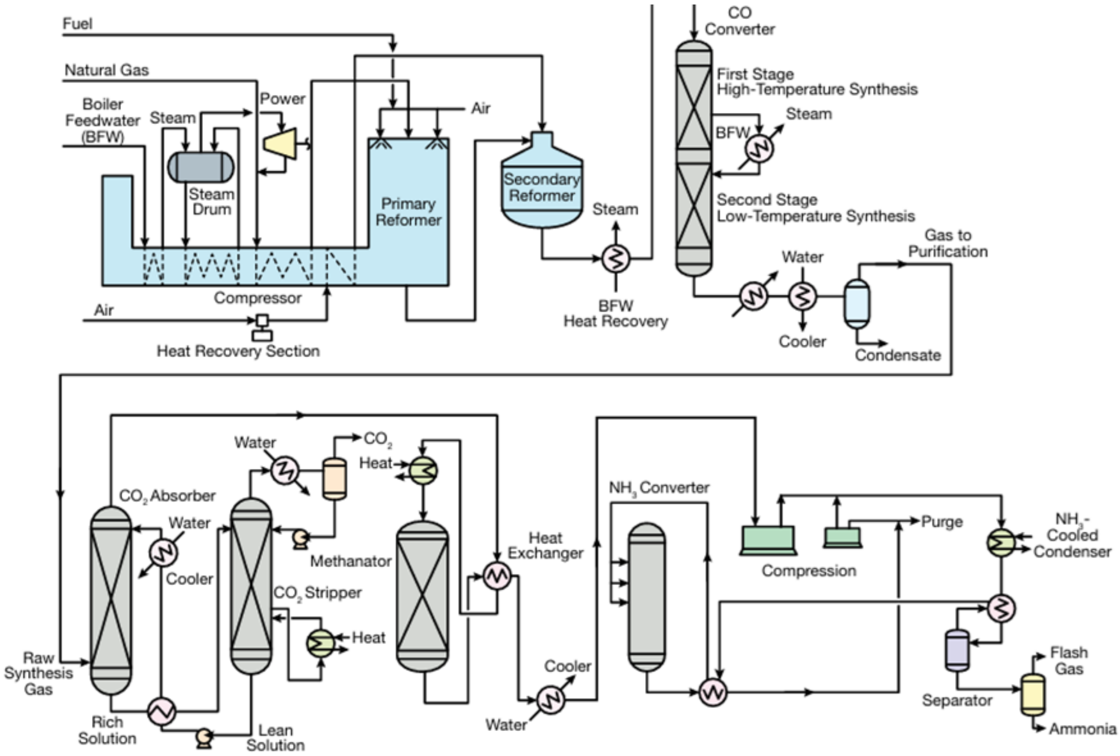


Figure 11. A single concept design of M.W. Kellog (Richardson & Pattabathula, 2016).

Larger capacity plants were needed to produce ammonia in 2000s. A lot of studies had been carried out for the use of many new technologies in ammonia production. Many of the new production plants have been designed using the method developed by the German chemist Fritz Haber (Richardson & Pattabathula, 2016). The ammonia plant process designed by KBR (Kellogg Brown and Root) is shown in Figure 12. Many other ammonia production plants are designed according to the KBR Purifier process.

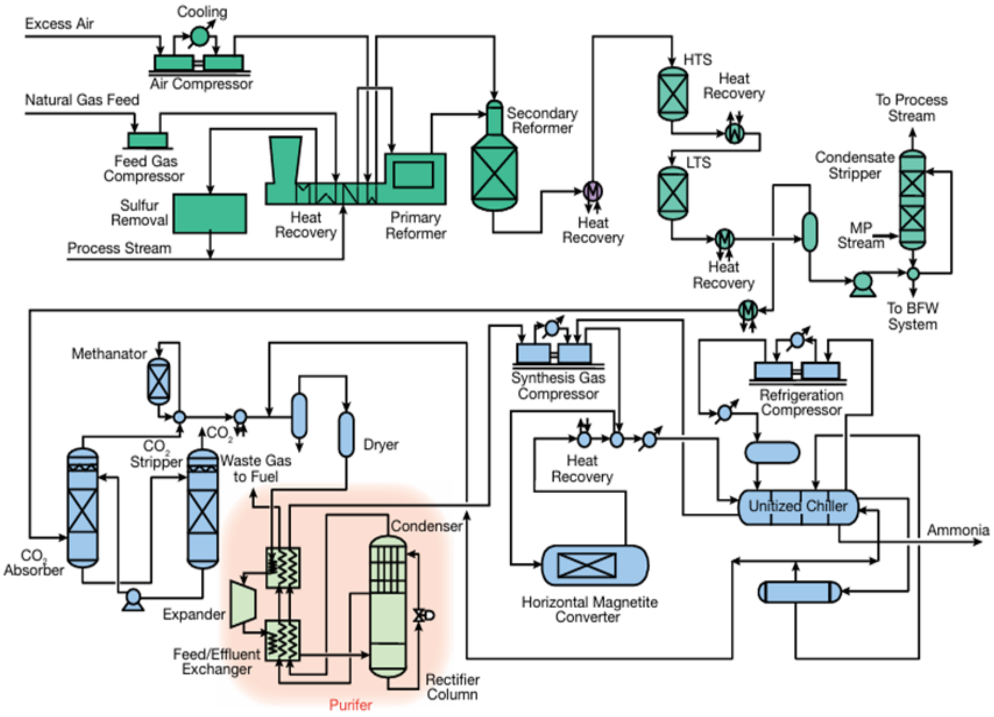


Figure 12. The model of purifier process to produce ammonia (Richardson & Pattabathula, 2016).

In the Haldor Topsøe model, iron-based synthesis catalyst, radial flow converters, and bayonet type waste heat boiler are used (Richardson & Pattabathula, 2016). The model designed by Haldor Topsøe is shown in Figure 13.

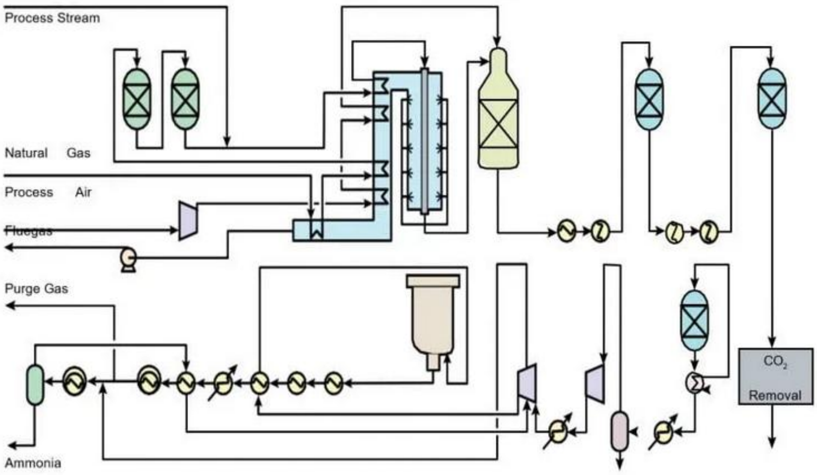


Figure 13. An ammonia design model of Haldor Topsøe (Richardson & Pattabathula, 2016).

A dual pressure ammonia production synthesis model designed by Thyssen Krupp is shown in Figure 14. In this production model, the radial flow converters of the waste heat boiler and the dual-pressure ammonia synthesis cycle are used. One of the most important goals of modern ammonia production plants today is to develop ammonia production with renewable technologies and start the use of CCS (Richardson & Pattabathula, 2016).

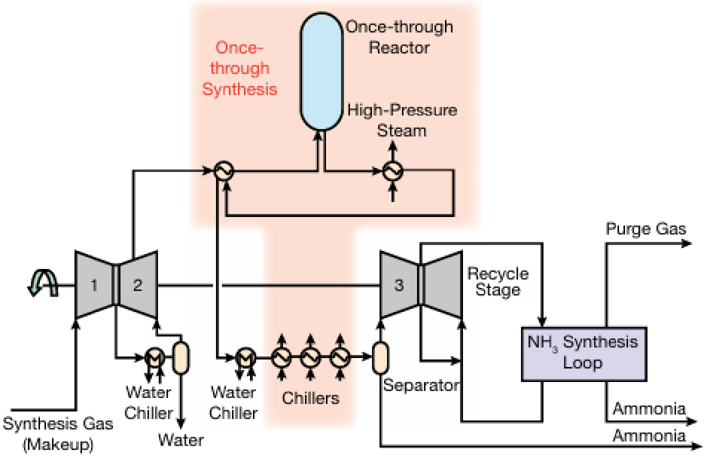


Figure 14. The dual pressure ammonia synthesis loop model of Thyssen Krupp (Richardson & Pattabathula, 2016).

4 Ammonia classifications

Many production methods have been implemented throughout history to minimize the impact of ammonia production on the environment. While making these evaluations, colors and classifications were made according to the impact of production on the environment and the emission values occurred in production. LCA can be used in evaluating the impact of the developed technology when the aim is to reduce CO_2 emissions. Many production methods aiming in CO_2 reduction have been developed for ammonia production, and they are electrolysis, pyrolysis, coal with CCS and gas with CCS. The carbon capture and utilization, CCU is referred to as CO_2 capture in the industry. CCU technologies could capture 90% of produced carbon via compression, transport, and underground storage solutions. In the world, nearly 0.03% of hydrogen production is done via electrolysis. Other electrolysis types are alkaline electrolysis (AE), polymer electrolyte membrane electrolysis (PEM) and solid oxide electrolysis (SOE) which is at development stage. (Boyce et al.,2024)

Hydrogen is classified according to its production method and process. These classifications are green hydrogen from renewable sources, grey hydrogen from fossil resources and blue hydrogen, which is also produced from fossil fuels but the process includes carbon capture and storage. In other words, CO_2 is stored in the blue hydrogen production. As hydrogen is required in ammonia production, ammonia is classified in the same way as hydrogen, based on the hydrogen manufacturing process. There are various pathways to produce hydrogen, shown in figure 15.

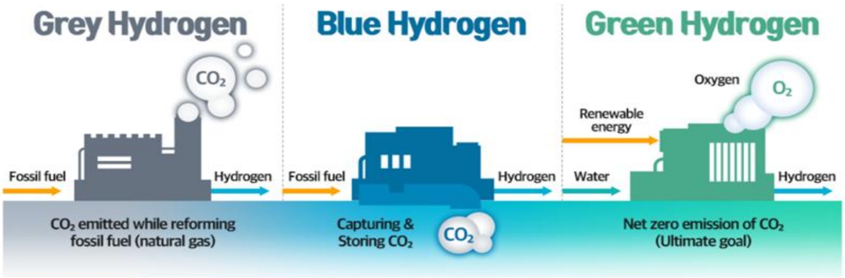


Figure 15. Hydrogen classifications according to production processes (Posco, 2020).

Green hydrogen production stages of one process are seen in Figure 16. Solar and wind energy are used as power source for electrolyzing water. Electrolysis produces hydrogen which is again synthetized to ammonia. This green hydrogen production model is modeled by POSCO which is steel company in the South Korea.

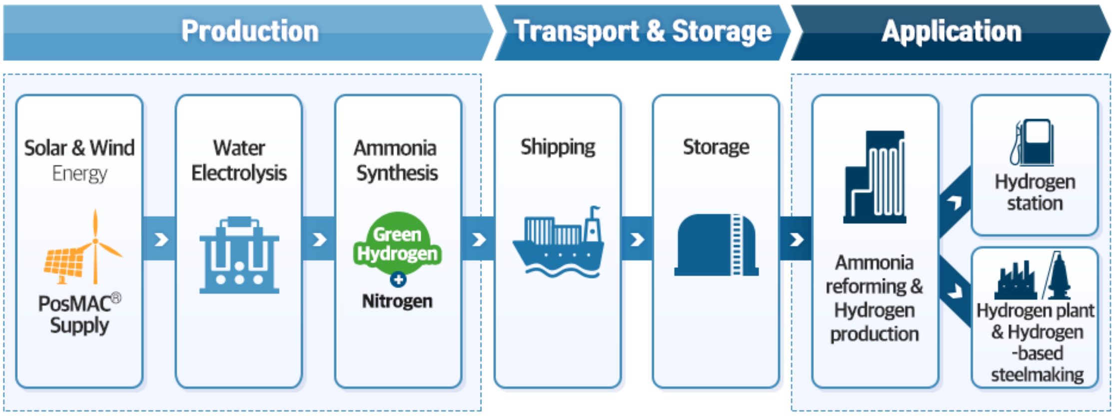


Figure 16. A green hydrogen production model of Posco (Posco, 2020).

4.1 Grey and black ammonia

Grey and black ammonia are produced from fossil fuels; the product is called grey if the raw material is natural gas and black if the raw material is coal or lignite. Natural gas is the most important raw material for the production, mainly due to its high methane density. The most of ammonia production is ensured from natural gas globally. The emissions that may occur in the production of grey ammonia are shown in Figure 17.

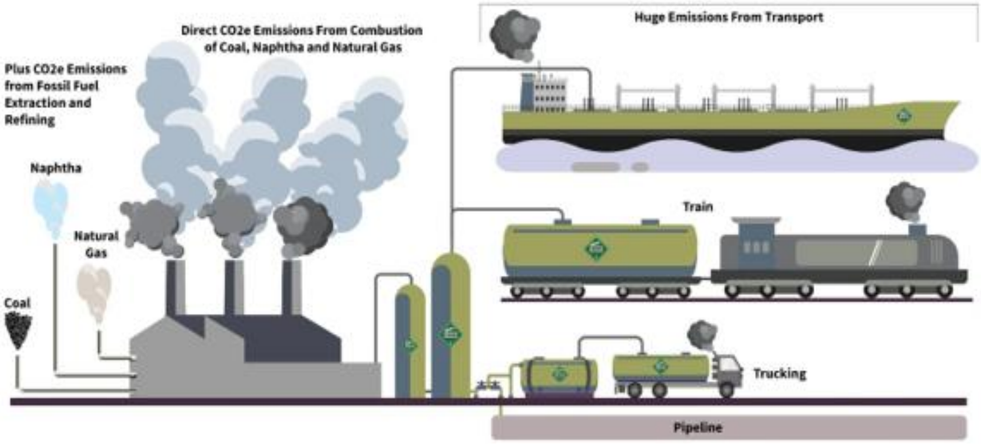


Figure 17. Grey ammonia production process (FuelPositive, n.d).

Ammonia production consumes 2% of all the fossil fuels in the world. Global ammonia production stands for the total energy consumption of approximately 2% that is nearly 8.6 EJ (exajoule). Of the existing ammonia production approximately 70% is grey and 30% is black ammonia. The grey ammonia production amount requires almost 170 billion cubic meters of natural gas which is 20% of the industrial natural gas demand. Also, there is a need for 75 million tons of coal for ammonia production which responds to 5% of industrial coal demand. (IEA, 2021) A comparison of the amount of emissions resulting from ammonia production in the world with other industrial products produced is shown in Figure 18.

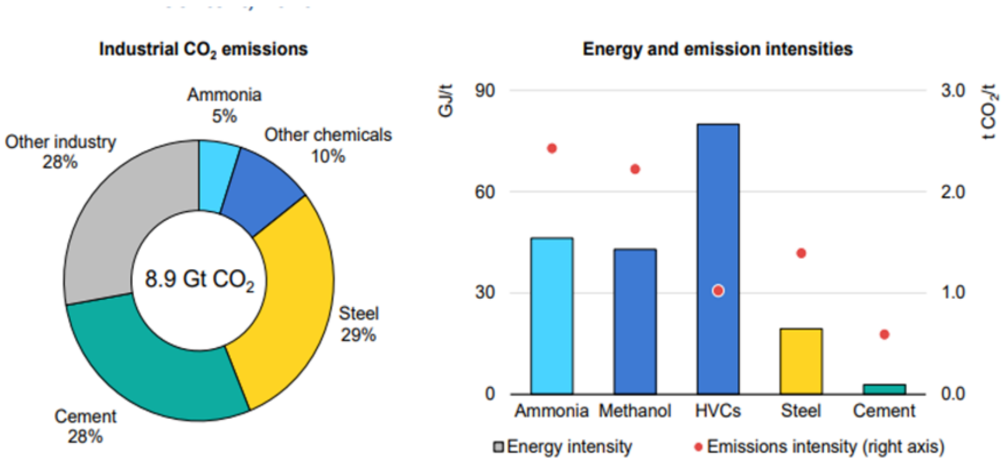


Figure 18. Industrial CO_2 emissions and energy emissions intensities (IEA, 2021).

Most of the produced ammonia at the moment is grey ammonia. The goal is to reduce the use of fossil fuels before the year 2050. For this reason, many new studies are made aiming to find replacement for the use of fossil fuels.

4.2 Blue ammonia

Blue ammonia is produced from fossil fuels, but CCS technology is applied to reduce the amount of CO_2 emissions in blue ammonia production. A schematic model for blue ammonia is shown in Figure 19, based on KBR production process. KBR that is American company who is producing blue ammonia. (Kellogg Brown & Root). In the production, either natural gas or other hydrocarbon feedstock or renewable energy as used as sources material. Blue ammonia production covers almost 1.8% of carbon dioxide emissions globally (KBR, 2023).

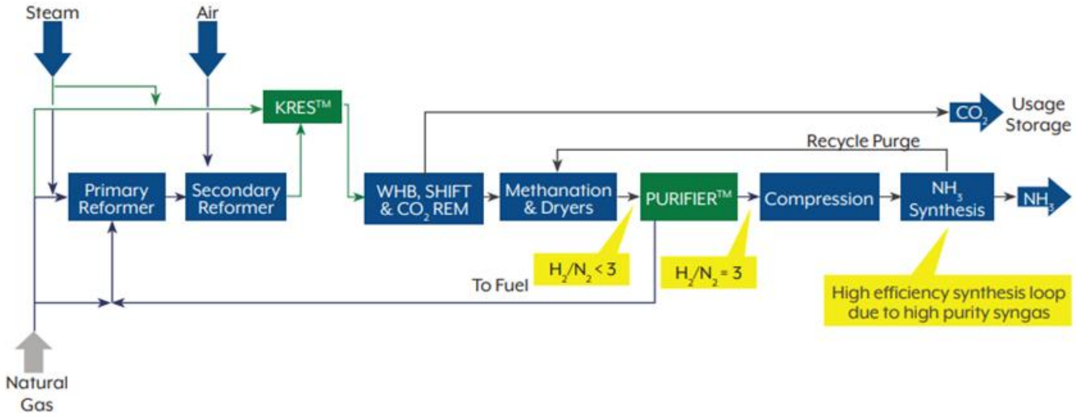


Figure 19. Schema created for blue ammonia production (KBR, 2023).

4.3 Green ammonia

Green ammonia production has a key role in cutting down the emissions of either food production or in energy industry. In green ammonia production, hydrogen is produced from renewable sources or using renewable technologies, which means that hydrogen is produced carbon-free. The production pathway of green ammonia is shown in Figure 20 (Iberdrola, n.d).

In green ammonia production hydrogen is produced via electrolysis of water. In other words, water is separated to oxygen and hydrogen using electrical energy obtained from renewable energy. Green hydrogen can also be produced by biomass gasification. Produced green hydrogen is then combined with atmospheric nitrogen using the Haber-Bosch process, which allows nitrogen and hydrogen to react at high temperature and pressure with the help of a catalyst. Ammonia is received as the end product of this process (Iberdrola, n.d).

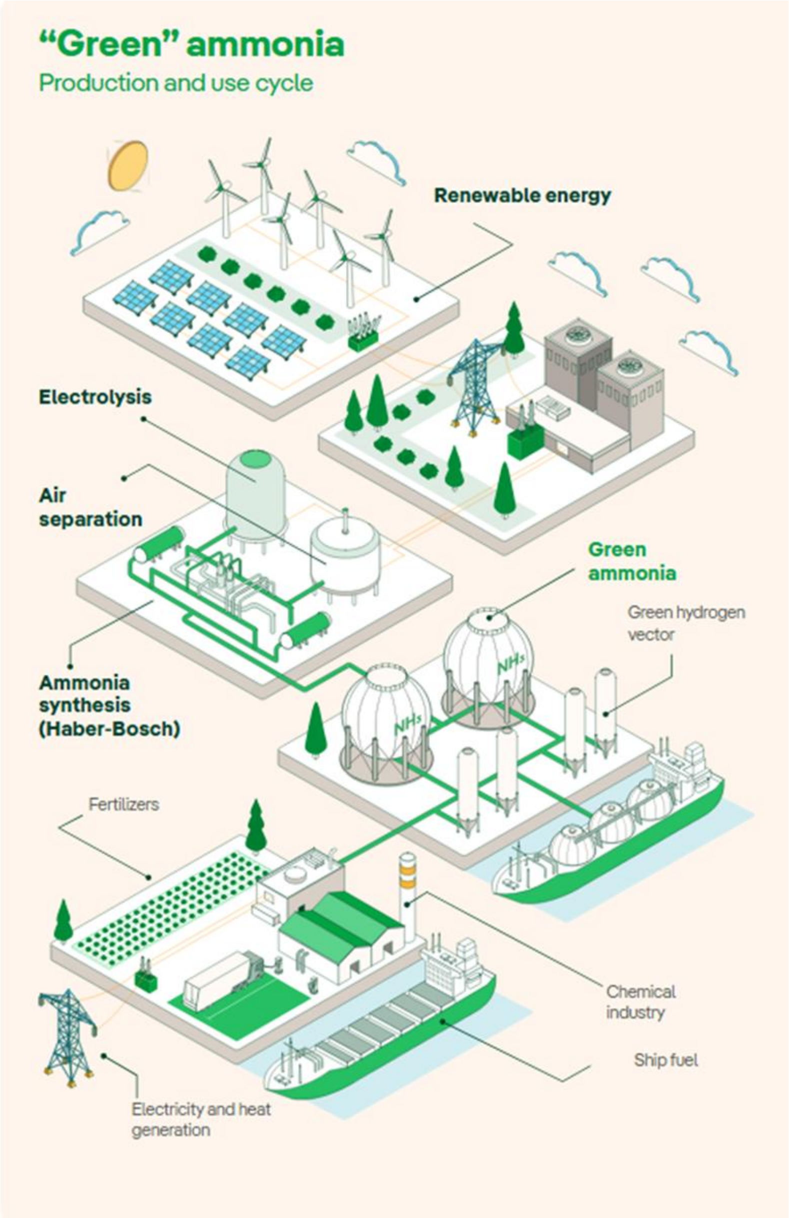


Figure 20. A production pathway for green ammonia (Iberdrola, n.d).

Green ammonia production integrates water electrolysis with the Haber-Bosch process. During electrolysis, electricity splits water molecules into hydrogen and oxygen. This occurs in cells with two electrodes separated by an electrolyte, which facilitates ion transfer (anions or cations). Electrolysis methods include alkaline water electrolysis (AWE), proton exchange membrane (PEM) electrolysis, solid oxide electrolysis (SOE), and microbial electrolysis cells (MEC). Nitrogen is supplied via an air separation unit (ASU). The process, reliant on renewable power, combines electrolyzers with the Haber-Bosch process, as illustrated in Figure 21 (Tornatore et al., 2022).

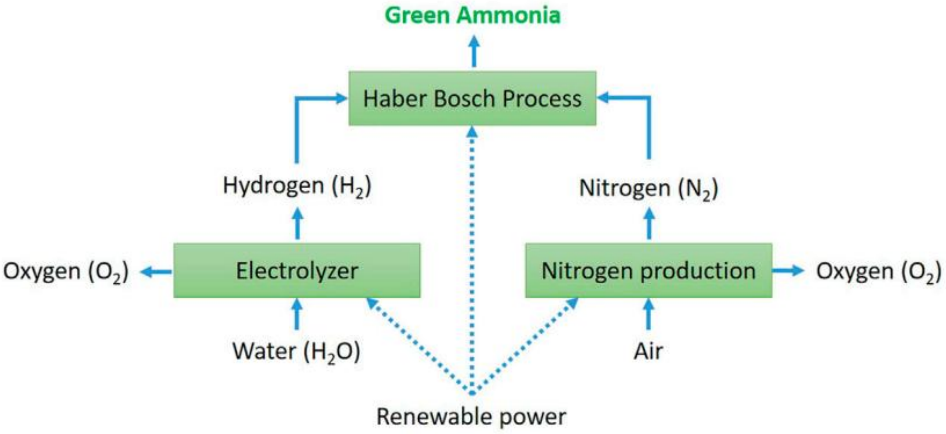


Figure 21. Electrolysis of water method to produce ammonia via green energy sources (Tornatore et al., 2022).

4.3.1 Renewable energy in ammonia production

Green hydrogen and ammonia are produced by utilizing renewable energy systems. A combination of biomass gasifier, solar heat, and a power generation system is used to increase the production of green fuels. Renewable ammonia has a very small part in the production which is 0.01% of global production today (Lefferts et al.,2022).

In renewable ammonia production, renewable power is used to separate water into hydrogen and oxygen via electrolysis. However, although there have been significant advances in the development of renewable ammonia production, it is not at the intended level. The total electrolyser capacity globally was approximately 500 Megawatts in 2021. To achieve net zero emissions in ammonia production, more than one megawatt energy would be needed to cover the energy demand in the production which is two times of the year 2021 capacity (Young et al.,2023).

A scenario of the resources needed for ammonia production has been created by Ammonia energy in 2019. The scenario up to 2050 is shown in Figure 22. According to this scenario, the aim is to increase the ammonia capacity produced from green energy significantly before 2050.

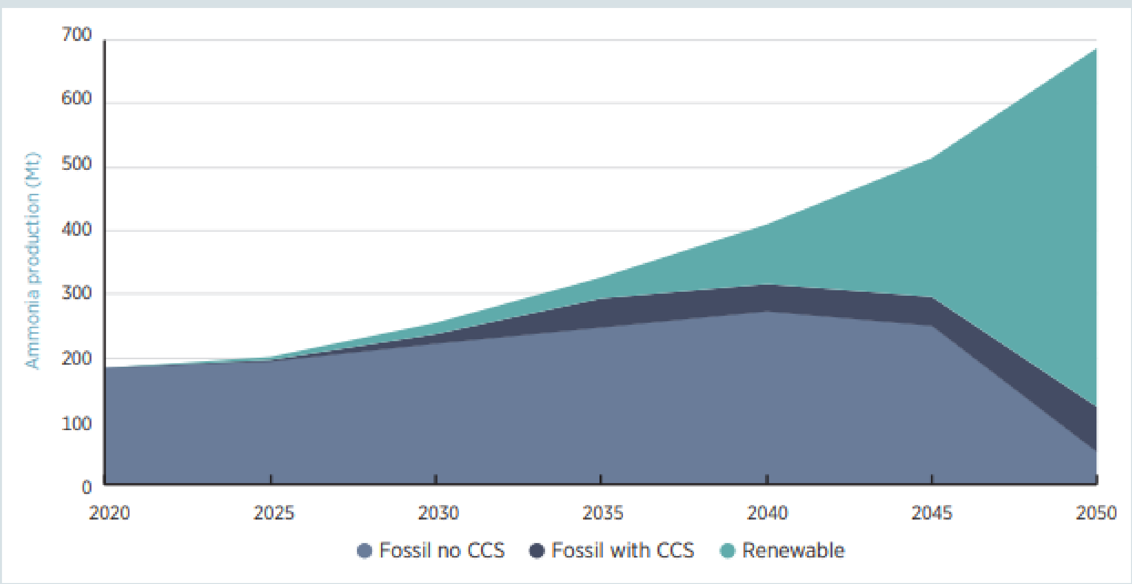


Figure 22. Scenario of resources to be increased in production until 2050 (Irena, 2022).

4.3.2 Biomass gasification in ammonia production

Green hydrogen and green ammonia can also be produced by gasifying biomass. This process was developed to produce a high H_2 content syngas. The process was tested on the Fast Internal Circulating Fluidised Bed (FICFB) gasifier at Gussing, in Austria. Biomass is dried after harvesting and planting. The next step of the process is biomass gasification with vapor oxidant, char burning in air and syngas cleaning. Hydrogen is obtained when CO_2 is removed and can be used for ammonia synthesis after that. (Gilbert et al. 2010) A schematic model of biomass gasification was created by Technical University of Vienna and the created model is shown in Figure 23.

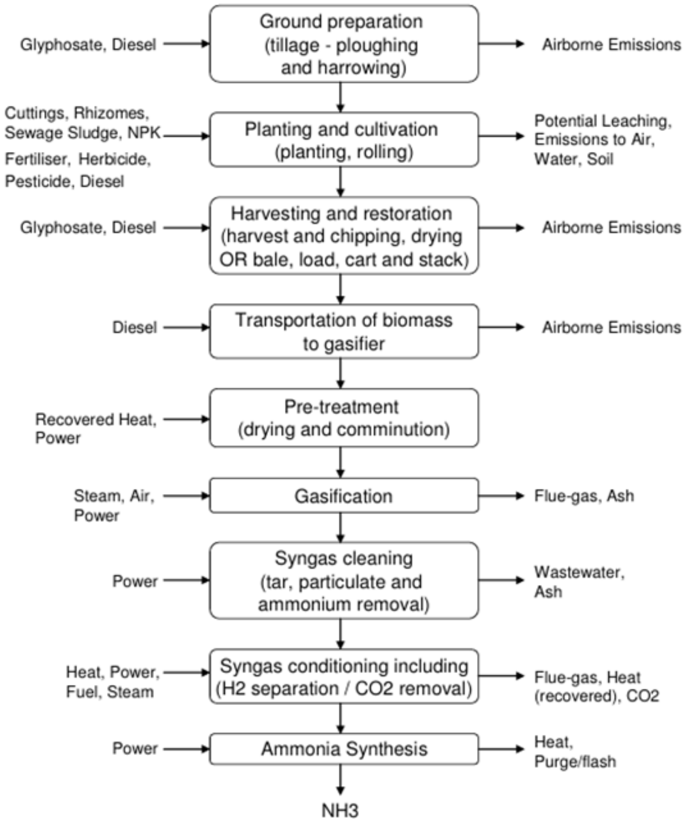


Figure 23. Biomass gasification schematic for ammonia production (Gilbert et al., 2010).

4.4 Turquoise ammonia

In turquoise ammonia production methane pyrolysis is carried out with solid carbon and CO_2 is not released. Natural gas, which is mostly used as raw material in ammonia production in the world, is preferred. Hydrogen and ammonia productions are carried out with a process also called methane pyrolysis, which is an effective process in separating natural gas from carbon. The zero CO_2 emission production is targeted in this process (Coleman, 2024).

5 Green ammonia production In Finland

Flexens Oy Ab is planning to develop a 300-megawatt green hydrogen and ammonia production plant at Kokkola Industrial Park, positioning it as one of Finland's largest ammonia projects. The initiative aims to reduce emissions and enhance Finland's self-sufficiency in energy and ammonia production, significantly contributing to the country's sustainable energy transition. The plant is expected to be operational by 2028, marking a key milestone in Finland's green energy landscape (Flexens, n.d.).

Plug Power, an American company, plans to develop three green hydrogen production plants in Finland, targeting a total output of 850 tons of green hydrogen per day by 2030, supported by 2.2 gigawatts of electrolyzer capacity. A final investment decision is anticipated by 2025 or 2026. The plants will utilize Proton Exchange Membrane (PEM) electrolyzers and liquefaction technology to produce hydrogen for ammonia and green steel production, aiding Europe’s decarbonization goals (Plug Power, 2023).

Green North Energy has completed the design for a scalable plant focused on producing green hydrogen and ammonia. With a capacity of 280 MW and a total investment of EUR 580 million, the plant aims to contribute to sustainable hydrogen and ammonia production. Set to begin operations in 2026, this state-of-the-art facility represents a significant advancement in sustainable ammonia production (Green North Energy, n.d.).

6 Ammonia as a fuel

Ammonia is being explored as a clean fuel alternative for shipping to help achieve decarbonization goals in the maritime sector, offering a sustainable solution for reducing emissions. Several companies have studied the use of ammonia in internal combustion engines. The most significant advantage of using it as fuel is that its emission value is almost non-existent. Another advantage of using ammonia as fuel is that it does not contain molecular carbon, which means that CO_2 emissions do not form when ammonia is used as fuel. Ammonia is a clean marine fuel, but it requires a larger fuel storage capacity compared to Marine Diesel Oil (MDO) or Liquefied Natural Gas (LNG). Ammonia has a lower volumetric energy density compared to conventional fuels. The first ammonia-powered ship was the Yara Eyde, which began operating in 2023 following a collaboration between North Sea Container and Yara International. The first voyage of the vessel was between Norway and Germany (Yara International, 2023). The Yara Eyde vessel is shown in Figure 24.

Figure 24. The first container ship which uses ammonia as fuel (Yara International, 2023).

Wärtsila conducted several trials on the use of ammonia as a fuel in 2022. Wärtsila announced the first trial results of ammonia fuel for their customers, specifically related to the 4-stroke engine. The engine, named Wartsila 25, was developed for these trials. The goal of using ammonia as fuel is to reduce the dependence on fossil fuels in engines and promote the use of an environmentally friendly fuel in maritime transportation (Alder, 2023). The Wartsila 25 engine, tested with ammonia fuel, is shown in Figure 25.

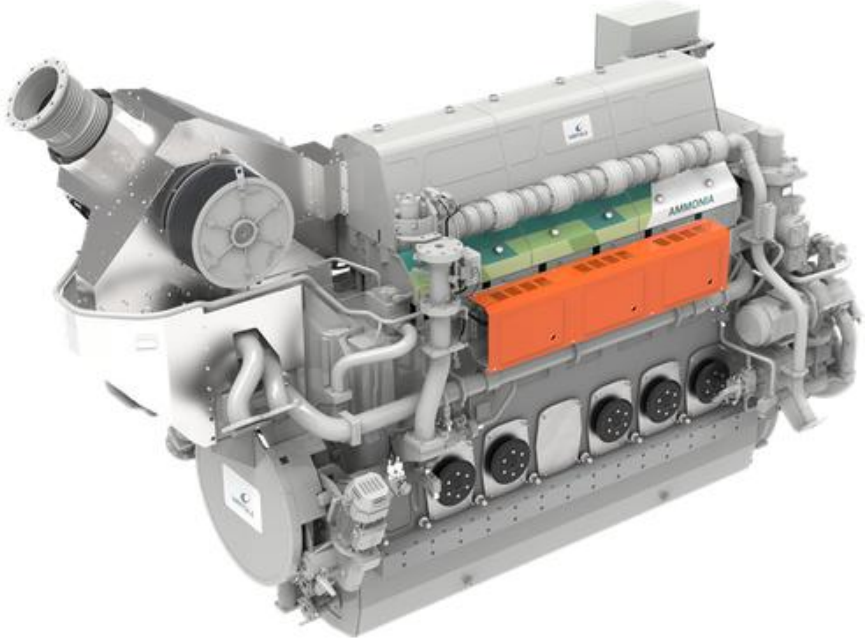


Figure 25. The first ammonia fueled engine of Wartsila (Wartsila 25) (Alder, 2023).

When ammonia is used as fuel, CO_2 does not form. Unburned ammonia escaping from the exhaust gases into the environment is referred to as ammonia slip. Along with NOx and N_2O, which form during ammonia combustion, ammonia slip can pose hazards and health risks to the crew working on the vessel and to local people at the ports. These substances also have a negative impact on the environment (Møller Center, 2023).

NOx emissions are a drawback of using ammonia as fuel in internal combustion engines. After-treatment technology is required to meet the defined NOx limits in dual-fuel ammonia engines. Several technologies, such as selective catalytic reduction (SCR) and exhaust gas recirculation (EGR), are used to reduce NOx emissions (Møller Center, 2023). The emissions from ammonia combustion and their impact on health, safety, and climate are shown in Figure 26.

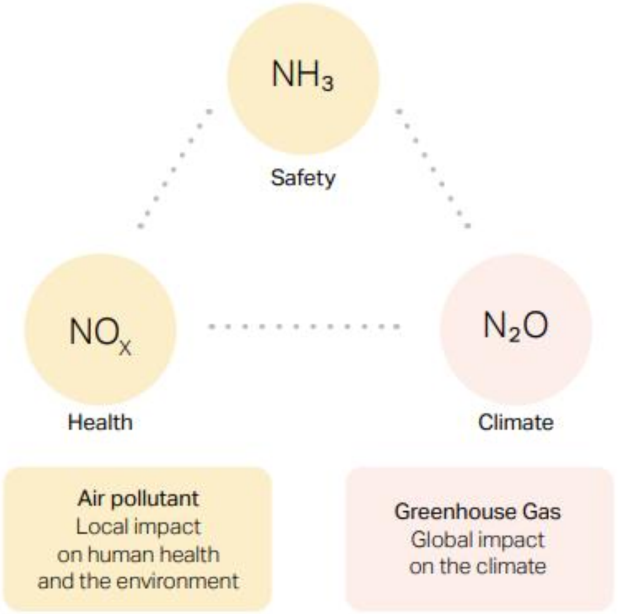


Figure 26. The emissions of ammonia combustion and the impact they have for health, safety and climate (Møller center, 2023).

7 Material and methods

This thesis uses the life cycle assessment (LCA) method to calculate the greenhouse gas (GHG) emission through the ammonia value chain. LCA is a standardized method for evaluating the possible environmental effects of a product throughout its life cycle. The most important standards for LCA are ISO 14040 and ISO 14044. *ISO 14040 outlines the principles and framework for LCA,* while ISO 14044 provides specific technical requirements and guidelines for LCA (Finkbeiner et al.,2006).

In the assessment, data on GHG emissions were collected for all processes in the life-cycle chain of ammonia, including extraction, pretreatment and transportation of raw materials, ammonia production and distribution, and finally, combustion in a marine engine (Fig. 27).

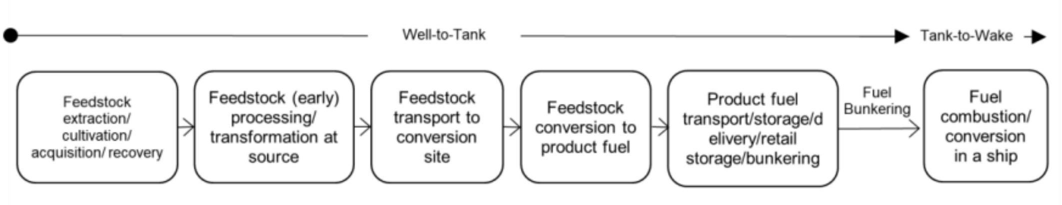


Figure 27. General life-cycle chain for marine fuels (IMO, 2024).

Several supply and production chains were evaluated for both fossil fuel-based and renewable energy-based ammonia production. The studied ammonia value chains are described in Section 7.1, and Section 7.2 gives details of GHG calculations for each fuel chain.

7.1 Ammonia value chains

7.1.1 Grey ammonia

In grey ammonia production, natural gas is used as a feedstock. To produce one tonne of anhydrous ammonia, 34.4 MMBtu (35 848 MJ) of natural gas is needed (Fielden, 2012).

Natural gas is delivered from USA (Texas) and ammonia production is performed in Finland (Helsinki). The distance between Texas and Helsinki is approximately 10930 km.

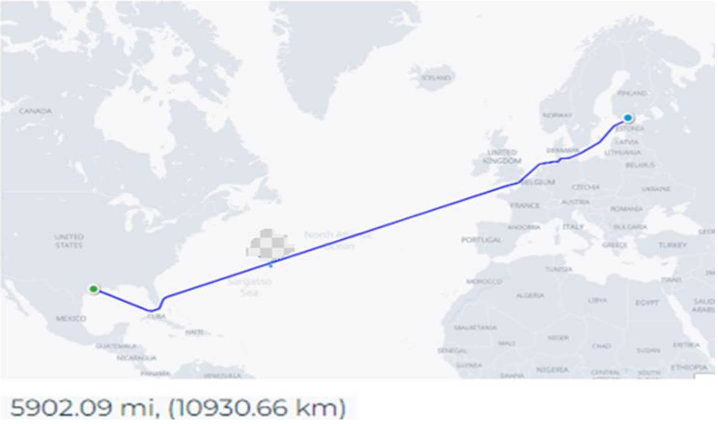


Figure 28. Overseas shipping route of natural gas.

Natural gas is supplied from Texas to Helsinki in liquefied form (LNG, liquefied natural gas) by a tanker ship. Two different fuels were used for overseas transportation: LNG and marine diesel oil (MDO). GHG emissions from overseas transportation were determined for both fuels following the IMO guidelines, explained in Section 7.2.

In the following step, the hydrogen needed in the ammonia synthesis is extracted from natural gas with steam methane reforming (SMR) process. In the SMR process, methane obtained from natural gas is heated with steam with the presence of a catalyst at a pressure of 3-25 bar. At the end of this process, hydrogen and carbon monoxide and are formed according to the reaction: $CH_4 + H_2O\ (+heat) \rightarrow CO + 3H_2$. The process is endothermic, meaning that heat is needed for the reaction to take place. (Studentenergy, n.d) The produced syngas is further treated in a water-gas shift reactor, where CO reacts with steam to produce additional hydrogen according to reaction $CO + H_2O \rightarrow CO_2 + H_2$. Hydrogen produced with SMR is then reacted with nitrogen using the Haber-Bosch method to produce ammonia.

The produced ammonia is transported to ports within a 100-kilometer radius and used as fuel for ships. Emissions during bunkering were not taken into account because there is not enough data related to ammonia bunkering available. The grey ammonia value chain is summarised in Figure 29.

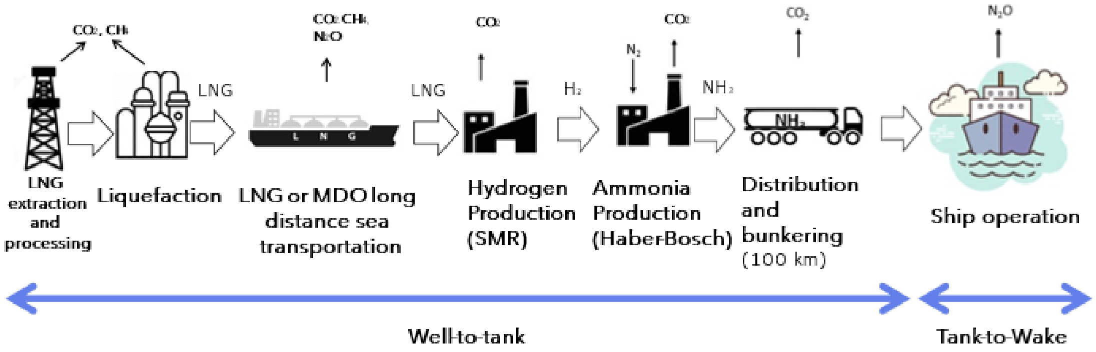


Figure 29. LCA model of grey ammonia production.

7.1.2 Blue ammonia

In the blue ammonia production process, the extraction and pretreatment, including liquefaction of natural gas, and LNG transportation from Texas to Helsinki by tanker ship are exactly the same as with grey hydrogen described above. The hydrogen production using SMR and the ammonia production via the Haber-Bosch method are similar to grey hydrogen, with the difference that in blue ammonia production, these processes are equipped with carbon capture and storage (CCS) process. Due to the implementation of the CCS system, CO_2 emissions are significantly reduced. Two different carbon capture rates were used: 60 and 90 %. The LCA model created for blue ammonia production is shown in Figure 30.

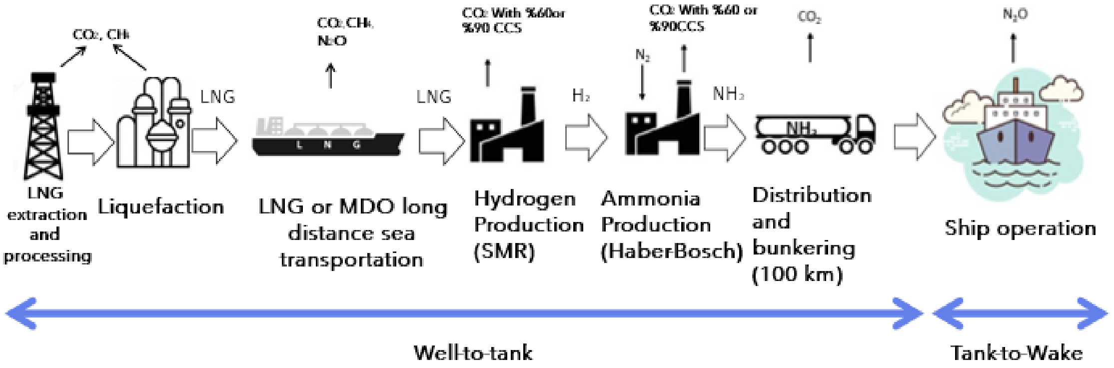


Figure 30. LCA model of blue ammonia production.

7.1.3 Green ammonia from electrolysis-based hydrogen

In green ammonia production, hydrogen is produced by electrolysis of water. The basic principle of electrolysis is to split water into oxygen and hydrogen, and for this process, direct current is passed through the water between two electrodes. The electrodes used for this process must be resistant to corrosion, have sufficient electrical conductivity and good catalytic properties, and the entire process must have appropriate structural integrity (Sanchis et al., 2012). The electricity needed for electrolysis is obtained from renewable sources. Hence, hydrogen production causes zero GHG emissions because the green energy sources don’t have any carbon compounds.

The produced hydrogen is stored, and the stored hydrogen is later used in ammonia production. Hydrogen storage can be made in gas or liquid form. High-pressure tanks are generally used to store hydrogen as a gas. Pressures varying between 350 and 750 atm are needed to store hydrogen gas. Cryogenic temperatures are required to store hydrogen as a liquid because the boiling point of hydrogen at atmospheric pressure is -252.8°C. The storage of hydrogen can also be performed on the surfaces of solids or inside solids. (U.S. Department of Energy, n.d)

Ammonia production is performed through the Haber-Bosch method. The energy needs of Haber-Bosch are also covered by renewable energy, such as wind power. The LCA model created for green ammonia production is shown in Figure 31.

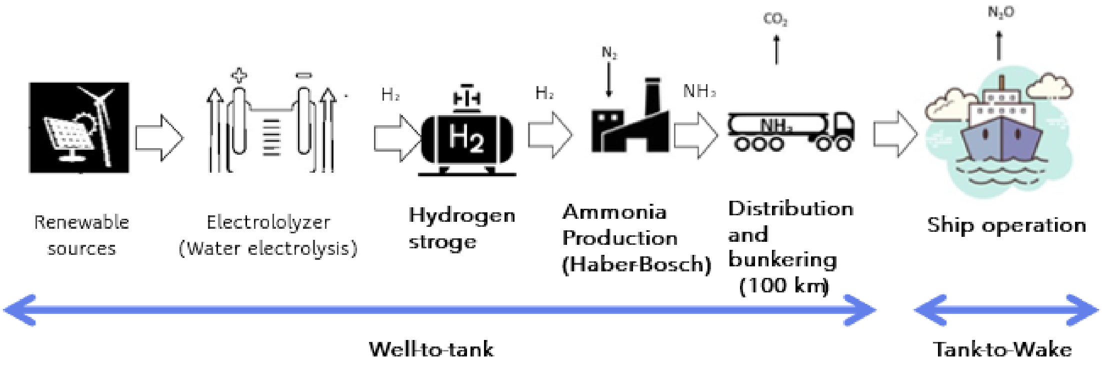


Figure 31. LCA model of green ammonia production.

7.1.4 Green ammonia from biomass

Ammonia from biomass can also be classified as green ammonia if the energy used in the process is from renewable sources. In this study, forest residues are used in biomass ammonia production. Transportation of forest residues is carried out from Lahti to Helsinki (120 km) and ammonia is produced in Helsinki. The feedstock is brought from Lahti to Helsinki by road trucks. The empty weight of the truck is 16 tonnes, and the maximum permissible weight of a seven-axle trailer combination In Finland is 60 tonnes (Logistiikan Maailma, n.d).

The hydrogen needed in ammonia synthesis is obtained from biomass via a gasification process, a controlled process involving heat, steam, and oxygen to convert biomass into hydrogen-rich syngas without combustion. To produce one ton of ammonia, 1.3–2.7 tons of biomass feedstock is needed (Gabrielli et al., 2023). This study uses an average of 2 tons of woody biomass per 1 ton of ammonia. Syngas from gasification, containing hydrogen and CO, is further treated with water in the water-gas shift reactor to produce additional hydrogen from CO. Hydrogen is then fed into the Haber-Bosch process, where it reacts with nitrogen to produce ammonia. The produced ammonia is transported to ports within a radius of 100 kilometers and used as fuel for ships. The LCA model created for biomass ammonia production is shown in Figure 32.

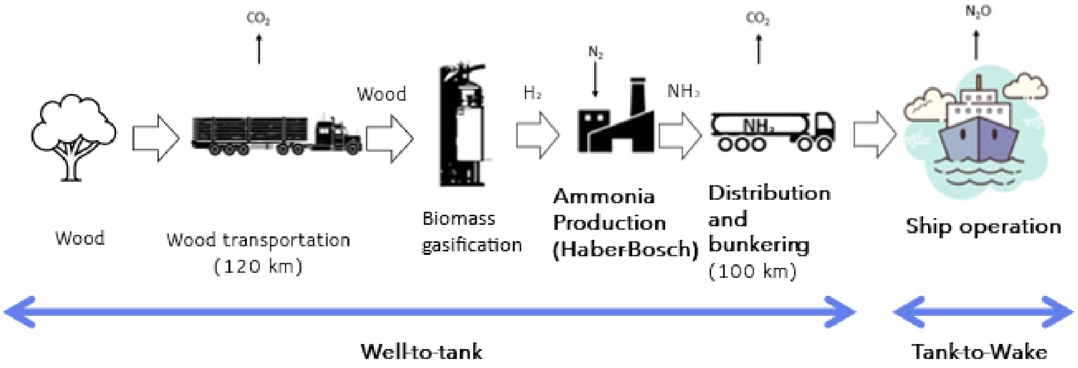


Figure 32. LCA model of ammonia production from biomass.

7.2 GHG calculations

The GHGs investigated in this study were CO_2, methane (CH_4) and nitrous oxide (N_2O). The total GHG emissions for each ammonia value chain are presented in terms of CO_2-equivalents, using 100-years global warming potential factor of 1 for CO_2, 29.8 for CH_4, and 273 for N_2O (Table 1) in accordance with the Intergovernmental Panel on Climate Change (IPCC) sixth assessment report (AR6). The functional unit, i.e. the reference unit against which life-cycle inventory data is calculated used in this study was grams of CO_2-equivalents per MJ of ammonia (gCO_2-eq./MJ_{NH3}).

Table 1. Global warning potential values according to IPCC AR6 (EcoOnline, n.d).

Greenhouse gas	**Global Warning Potential (GWP100)**
Carbon dioxide (CO_2)	1
Methane (CH_4)	29.8
Nitrous oxide (N_2O)	273

In the GHG calculations, the following stages were considered, in line with the IMO LCA guidelines (IMO, 2024):

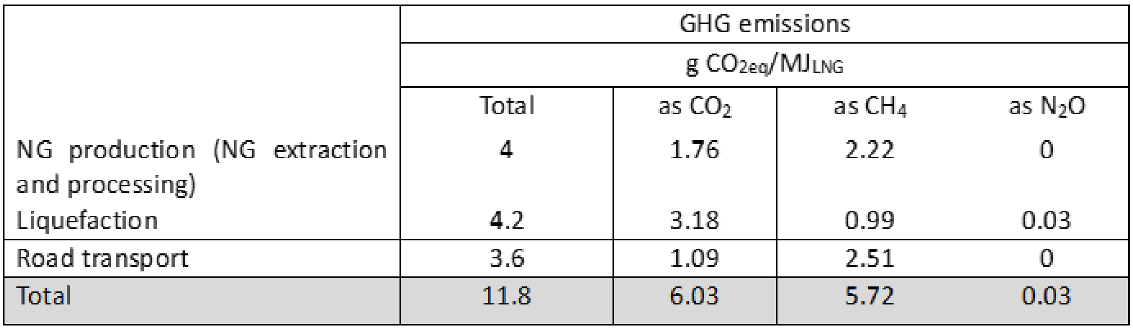
- feedstock extraction
- feedstock preprocessing
- feedstock transportation to the conversion site
- feedstock conversion into fuel
- distribution of the produced fuel
- and finally, its use as fuel on ships

The five first steps are commonly referred to as well-to-tank (WtT) phase, and the final use, i.e., combustion in a marine engine, is referred to as tank-to-wake (TtW) phase. Together, these phases form well-to-wake (WtW) phase.

7.2.1 GHG emissions from LNG production

GHG emissions from natural gas extraction, processing to LNG, and transportation to the departure port were retrieved from (Prussi et al., 2020) and shown in Table 2 below. The total GHG emissions from LNG production is 11.8 g CO_2-eq./MJ_{LNG}.

Table 2. Total GHG emission from LNG production (Prussi et al., 2020).



	GHG emissions			
	g CO_{2eq}/MJ_{LNG}			
	Total	as CO_2	as CH_4	as N_2O
NG production (NG extraction and processing)	4	1.76	2.22	0
Liquefaction	4.2	3.18	0.99	0.03
Road transport	3.6	1.09	2.51	0
Total	11.8	6.03	5.72	0.03

7.2.2 GHG emissions from feedstock transportation

Overseas transportation

Two types of fuels were considered for LNG overseas transportation: MDO and LNG. The total engine power of the tanker ship used in LNG overseas transportation is 24 980 kW. In MDO mode, the specific fuel consumption (SFC) of the main engine (ME) is 0.165 kg/kWh, and the auxiliary engine (AE) 0.187 kg/kWh. The corresponding values in LNG mode are 0.136 kg_{LNG}/kWh and 0.160 kg_{LNG}/kWh. In LNG mode, MDO is used as a pilot fuel. Pilot fuel consumption of the main engine in LNG mode is 6 g_{MDO}/kWh, and auxiliary engine 7 g_{MDO}/kWh. Table 3 summarises the engine power and SFC data used in this study.

Table 3. Fuel consumption and the total power of the tanker ship engine (IMO, 2018).

$SFC_{ME\ MDO}$	0.165	kg/kWh
$SFC_{AE\ MDO}$	0.187	kg/kWh
$SFC_{ME\ LNG}$	0.136	kg/kWh
$SFC_{AE\ LNG}$	0.16	kg/kWh
Total power	24980	kW
$SFC_{AE\ pilot}$	0.007	kg_{MDO}/kWh
$SFC_{ME\ pilot}$	0.006	kg_{MDO}/kWh
Pilot fuel	73 334	kg_{MDO}

The engine power output was calculated assuming an average load of 75 % for the main engine and 5 % for the auxiliary engine, based on IMO (2018). With a speed of 19.5 knots (36.1 km/h), the duration of one round-trip is 605.3 h. So, the total power output for one round-trip could be determined as follows:

- Power output of main engine (P_{ME})= 24 980 kW*0.75*605.3 h = 11 340 296 kWh
- Power output of auxiliary engine (P_{AE})= 24 980 kW* 0.05*605.3 h = 756 020 kWh

The total fuel consumptions (in kg) were then calculated according to Equations 1 and 2.

$$MDO = P_{ME}\ x\ SFC_{ME\ MDO} + P_{AE}\ x\ SFC_{AE\ MDO} \qquad (1)$$

$$LNG = P_{ME}\ x\ SFC_{ME\ LNG} + P_{AE}\ x\ SFC_{AE\ LNG} + pilot\ fuel \qquad (2)$$

$$Pilot\ fuel = P_{ME} x SFC_{ME\ pilot} + P_{AE} x SFC_{AE\ pilot}$$

GHG emissions from one round trip were calculated based on the total fuel consumption and the IMO LCA guidelines' default tank-to-wake emission factors (C_f) (IMO, 2024), shown in Table 4. Emission calculations followed Equations 3 and 4.

Table 4. Emissions factors of MDO and LNG (IMO, 2024).

Type of fuel	**C_F (gCO_2/gFuel)**	**C_F (gCH_4/gFuel)**	**C_F (gCO_2/gFuel)**
MDO	3.206	0.00005	0.00018
LNG	2.750	ME 1.7 mass-% AE 3.5 mass-%	0.00011

$$GHG_{MDO} = \left(MDO x C_{f\ MDO}\right) + \left(MDO x C_{f\ CH_4} x\ 29.8\right) + \left(MDO x C_{f N_2 O}\ x\ 273\right) \quad (3)$$

$$GHG_{LNG} = \left(LNG x C_{f\ LNG}\right) + \left(P_{ME} x SFC_{ME} x \frac{1.7}{100} x 29.8\right) + \left(P_{AE} x SFC_{AE} x \frac{3.5}{100} x 29.8\right) + \left(LNG x C_{f N_2 O}\ x 273\right) + \left(pilot x C_{f\ MDO}\right) + \left(pilot x C_{f\ MDO} x 29.8\right) + \left(pilot x C_{f\ MDO} x 273\right) \quad (4)$$

To determine the greenhouse gas emissions of overseas transports in units of gCO_2-eq./MJ of ammonia, the total greenhouse gas emissions of one round trip were divided by the amount of ammonia obtained from LNG transported by one voyage.

Road transportation

The GHG emissions resulting from the transportation of raw materials needed for biomass ammonia production were calculated based on the following assumptions:

- The amount of feedstock needed for ammonia production 2 tons of biomass per 1 ton of ammonia
- Loading capacity of the truck 44 tons

- Fuel consumption of the truck 35 l/100 km
- Distance 120 km
- Diesel fuel density 0.805 kg/l (Fuel classification, 2024)
- Diesel LHV 42.8 MJ/kg (Fuel classification, 2024)
- Diesel emission factor 73.3 gCO_2/MJ (Fuel classification, 2024).

First, fuel consumption for one trip was calculated based on the information listed above. The fuel consumption (in MJ) was then multiplied by the emissions factor of 73.3 gCO_2/MJ of diesel fuel to get total GHG emissions per one trip. GHG emissions in gCO_2-eq./MJ of ammonia were obtained by dividing the total GHG emissions of one trip by the ammonia yield of one truckload.

7.2.3 GHG emissions from ammonia production

LCA evaluation was performed for four different variable ammonia production methods. As previously explained, these production methods are grey ammonia, blue ammonia, green ammonia from electrolysis-based hydrogen, and biomass ammonia. Emission calculations originating from ammonia production contain following stages:

- Steam reforming of methane (natural gas) + Haber-Bosch -> grey ammonia
- Steam reforming of methane + CCS + Haber-Bosch -> blue ammonia
- Water electrolysis + Haber-Bosch- > green ammonia
- Biomass gasification + Haber-Bosch -> biomass ammonia

Emission from SMR + Haber-Bosch

The emission value using standard steam methane reforming and Haber-Bosch process is approximately 1.5 to 2.0 kg CO_2 per kg of ammonia (Fazeli et al., 2020). This study uses an average of 1.75 CO_2/kgNH_3 for grey ammonia. For blue ammonia production, CO_2 capture rates of 90 % and 60 % were applied, resulting in GHG emission factors of
0.7 kgCO_2/kgNH_3 (CCS 60 %) and 0.175 kgCO_2/kgNH_3 (CCS 90 %).

A comparison of the energy input and emissions related to ammonia production is illustrated in Figure 33.

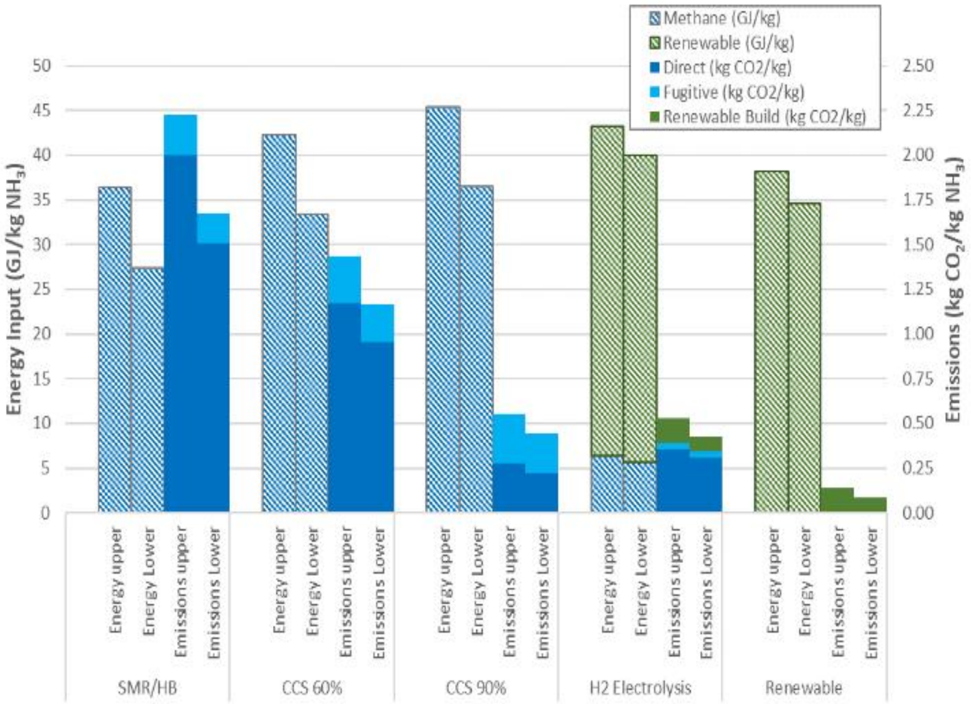


Figure 33. Energy input and GHG emissions related to ammonia production (Fazeli et al., 2020).

Water electrolysis + Haber-Bosch

The most basic need for green ammonia production from electrolysis-based hydrogen is electrical energy. In the case of electrolysis-based ammonia production, this study assumed that all energy needs associated with hydrogen production and Haber-Bosch are covered with renewable sources with zero GHG emissions.

Biomass gasification + Haber-Bosch

All the energy needs for biomass gasification and the Haber-Bosch process were assumed to be covered by renewable sources with zero GHG emissions. Hence, in the case of biomass ammonia, GHG emissions are only linked to the transportation of raw materials and the distribution and final use of ammonia.

7.2.4 GHG emissions from ammonia distribution

The calculation of GHG emissions from ammonia distribution was based on the following assumptions:

- Loading capacity of the truck 44 tons
- Fuel consumption of the truck 35 l/100 km
- Distance 100 km
- Diesel fuel density 0.805 kg/l, LHV 42.8 MJ/kg
- Emission factor for diesel fuel 73.3 gCO_2/MJ

To obtain GHG emissions in gCO_2-eq./MJ_{NH3}, the total fuel consumption of one trip was calculated first. The total fuel consumption (in MJ) was then multiplied by the emission factor of diesel fuel and divided by the mass of ammonia transported on one trip.

7.2.5 GHG emissions from ammonia end-use

Ammonia is a carbon-free fuel; hence, it doesn't produce CO_2 when combusted in a marine engine. However, ammonia contains nitrogen, and burning it is likely to result in nitrous oxide emissions. In this study, the N_2O emissions were assumed to be 0.000158 gN_2O/gNH_3, based on Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping (2023), corresponding to 2.32 gCO_2-eq./MJ of NH_3.

8 Results

8.1 Grey ammonia

Well-to-tank GHG emissions

At first, GHG emissions from LNG production were solved. The amount of LNG transported in one trip was 98 740 t. The GHG emission factor for LNG production is 11.8 gCO_2-eq/MJ_{LNG} (Table 2). On LHV-basis (50 MJ/kg of LNG), this corresponds to 590 gCO_2-eq./kg of LNG and 58 257 tCO_2-eq./voyage. The amount of ammonia that can be produced considering the ship's capacity was 113 903 tons of NH_3/voyage. Hence, the GHG emissions from LNG production are 0.511 tCO_2-eq./tNH_3.

The GHG emissions from LNG overseas transportation were calculated using two different fuel options. These calculations were made using the formulas specified by IMO and presented in Section 7.2. (Equations 3 and 4). In the MDO case, the total GHG emissions from one round-trip were 6 554 tCO_2/trip and 0.0575 tCO_2-eq./t_{NH3}. In the LNG case, corresponding values were 5 770 tCO_2/trip and 0.0507 tCO_2-eq./t_{NH3}.

The GHG emissions generated during ammonia production were 1 750 tCO_2- eq./t_{NH3}, and from ammonia distribution, 0.00201 tCO_2-eq./t_{NH3}.

Based on the above, the total well-to-tank emissions of grey ammonia in the LNG case were 2.314 tCO_2-eq./t_{NH3}, and in the MDO case, 2.321 tCO_2-eq./t_{NH3}. MJ-based emission values, 124.4 gCO_2-eq./MJ_{NH3} for the LNG case and 124.8 gCO_2-eq./MJ_{NH3} for the MDO case, were obtained by dividing the mass-specific emissions values by the LHV of ammonia (18.6 MJ/kg).

Well-to-wake GHG emissions

Finally, GHG emissions from ammonia end-use were added. GHG emissions from ammonia combustion in a marine engine were assumed at 2.3 gCO_2-eq./MJ_{NH3}, leading to the total well-to-wake GHG emissions of 126.7 gCO_2-eq./MJ in LNG case and 127.1 gCO_2-eq./MJ in MDO case.

Table 5 summarises the life-cycle GHG emissions of the grey ammonia value chain.

Table 5. Life-cycle GHG emissions of grey ammonia**.**

	LNG case	**MDO case**	**Unit**
CO_2-eq. from LNG production	0.511	0.511	tCO_2-eq. /t_{NH3}
CO_2-eq. from transport	0.0507	0.0575	tCO_2-eq. /t_{NH3}
CO_2-eq. from ammonia production	1.750	1.750	tCO_2-eq. /t_{NH3}
CO_2-eq. from ammonia distribution	0.00201	0.00201	tCO_2-eq. /t_{NH3}
Well-to-tank total	2.314	2.321	tCO_2-eq. /t_{NH3}
Well-to-tank total	**124.4**	**124.8**	**gCO_2-eq./MJ_{NH3}**
CO_2-eq. from end-use	2.3	2.3	gCO_2-eq./MJ_{NH3}
Well-to-wake total	**126.7**	**127.1**	**gCO_2-eq./MJ_{NH3}**

8.2 Blue ammonia

Well-to-tank GHG emissions

Well-to-tank GHG emission calculation of blue ammonia production begins with LNG supply and transportation. Emissions from LNG production and transportation have been described previously in the grey ammonia section.

The most important aspect to consider when calculating GHG emissions of blue ammonia is the use of CCS technology. The amount of GHG emissions generated during ammonia production in the CCS 60 % case was 79 732 tCO_2-eq./voyage, corresponding to 0.7 tCO_2-eq./t_{NH3}. When the CCS rate was increased to 90 %, emission value from ammonia production decreased to 19 933 tCO_2-eq./voyage, equating to 0.175 tCO_2-eq/t_{NH3}.

GHG emissions from ammonia distribution were 0.00201 tCO_2-eq./t_{NH3}. The total well-to-tank emissions of blue ammonia in MJ-basis in the CCS 60 % case were 68.0 gCO_2-

eq./MJ$_{NH3}$ (LNG ship) and 68.3 gCO$_2$-eq./MJ$_{NH3}$ (MDO ship). In the CCS 90 % case, the corresponding values were 39.7 gCO$_2$-eq./MJ$_{NH3}$ and 40.1 gCO$_2$-eq./MJ$_{NH3}$.

Well-to-wake GHG emissions

After adding the GHG emissions from ammonia end-use (2.3 gCO$_2$-eq./MJ$_{NH3}$), the total well-to-wake GHG emissions in the CCS 60 % case were 70.3 gCO$_2$-eq./MJ$_{NH3}$ (LNG ship) and 70.6 gCO$_2$-eq./MJ$_{NH3}$ (MDO ship). In the CCS 90 % case, the corresponding values were 42.1 gCO$_2$-eq./MJ$_{NH3}$ (LNG ship) and 42.4 gCO$_2$-eq./MJ$_{NH3}$ (MDO ship).

Table 6 summarises the GHG emissions of blue ammonia value chain with CCS 60 %, and the GHG emissions of blue ammonia value chain with CCS 90 % are shown in Table 7.

Table 6. Life-cycle GHG emissions of blue ammonia, CCS 60 %.

	LNG case	**MDO case**	**Unit**
CO$_2$-eq. from LNG production	0.511	0.511	tCO$_2$-eq. /t$_{NH3}$
CO$_2$-eq. from transport	0.0507	0.0575	tCO$_2$-eq. /t$_{NH3}$
CO$_2$-eq. from ammonia production	0.700	0.700	tCO$_2$-eq. /t$_{NH3}$
CO$_2$-eq. from ammonia distribution	0.00201	0.00201	tCO$_2$-eq. /t$_{NH3}$
Well-to-tank total	1.264	1.271	tCO2-eq. /t$_{NH3}$
Well-to-tank total	**68.0**	**68.3**	**gCO$_2$-eq./MJ$_{NH3}$**
CO$_2$-eq. from end-use	2.3	2.3	gCO$_2$-eq./MJ$_{NH3}$
Well-to-wake total	**70.3**	**70.6**	**gCO$_2$-eq./MJ$_{NH3}$**

Table 7. Life-cycle GHG emissions of blue ammonia, CCS 90 %.

	LNG case	**MDO case**	**Unit**
CO$_2$-eq. from LNG production	0.511	0.511	tCO$_2$-eq./t$_{NH3}$
CO$_2$-eq. from transport	0.0507	0.0575	tCO$_2$-eq./t$_{NH3}$
CO$_2$-eq. from ammonia production	0.175	0.175	tCO$_2$-eq./t$_{NH3}$
CO$_2$-eq. from ammonia distribution	0.00201	0.00201	tCO$_2$-eq./t$_{NH3}$

Well-to-tank total	0.739	0.746	tCO2-eq./t_{NH3}
Well-to-tank total	**39.7**	**40.1**	**gCO_2-eq./MJ_{NH3}**
CO_2-eq. from end-use	2.3	2.3	gCO_2-eq./MJ_{NH3}
Well-to-wake total	**42.1**	**42.4**	**gCO_2-eq./MJ_{NH3}**

8.3 Green ammonia from electrolysis-based hydrogen

In green ammonia production, hydrogen is produced via electrolysis of water, and the energy needed for the electrolysis of water is provided by green energy sources. Since neither the needed feedstock to produce green ammonia nor the energy used in the ammonia production process do not have carbon content, the amount of GHG emissions resulting from green ammonia production is zero. Hence, only the GHG emissions originating from ammonia distribution and end-use were considered. The total well-to-wake emissions of green ammonia were 2.4 gCO_2-eq./MJ of NH_3 (Table 8).

Table 8. Life-cycle GHG emissions of green ammonia produced from electrolysis-based hydrogen.

CO_2-eq. from ammonia production	0	tCO_2-eq. /t_{NH3}
CO_2-eq. from ammonia distribution	0.00201	tCO_2-eq. /t_{NH3}
Well-to-tank total	0.00201	tCO_2-eq. /t_{NH3}
Well-to-tank total	**0.108**	**gCO_2-eq./MJ_{NH3}**
CO_2-eq. from end-use	2.3	gCO_2-eq./MJ_{NH3}
Well-to-wake total	**2.4**	**gCO_2-eq./MJ_{NH3}**

8.4 Green ammonia from biomass

Well-to-tank GHG emissions

GHG calculations for green ammonia from biomass begin with feedstock collection and transportation. The amount of biomass feedstock transported in one trip is 44 tons. As stated before, the amount of biomass needed for ammonia production is 2 tons of biomass per 1 ton of ammonia. So, the amount of ammonia produced from 44 tons of raw material is 22 tons. With the assumption listed in Section 7.2.4, the GHG emissions of one round-trip are 0.212 tCO_2/trip, corresponding to 0.00964 tCO_2/t_{NH3} and 0.518 gCO_2/MJ_{NH3}.

Energy needs for biomass gasification and the Haber-Bosch process were assumed to be from renewable sources, and the GHG emissions from ammonia production were set at zero. After adding the GHG emissions from ammonia distribution (0.00201 tCO_2-eq./t_{NH3}), the total well-to-tank GHG emissions of biomass ammonia were 0.626 tCO_2-eq./MJ_{NH3}.

Well-to-wake GHG emissions

Like in the previous cases, the GHG emissions from the ammonia end-use were set at 2.3 gCO_2-eq./MJ_{NH3}. The total well-to-wake emissions were 2.9 gCO_2-eq./MJ_{NH3}. The results are summarized in Table 9.

Table 9. Life-cycle GHG emissions of green ammonia produced from biomass.

CO_2-eq. from feedstock transportation	0.518	gCO_2-eq./MJ_{NH3}
CO_2-eq. from biomass gasification + HB	0	tCO_2-eq. /t_{NH3}
CO_2-eq. from ammonia distribution	0.00201	tCO_2-eq. /t_{NH3}
Well-to-tank total	**0.626**	**gCO_2-eq./MJ_{NH3}**
CO_2-eq. from end-use	2.3	gCO_2-eq./MJ_{NH3}
Well-to-wake total	**2.9**	**gCO_2-eq./MJ_{NH3}**

8.5 Summary of results

The life-cycle GHG calculation results of different ammonia production pathways are summarised in Figure 34.

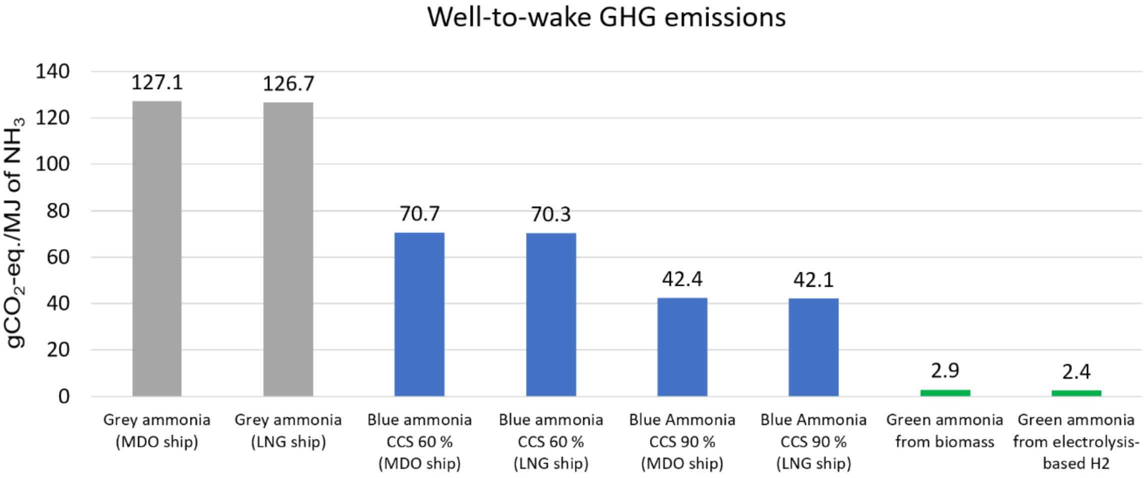


Figure 34. Well-to-wake GHG emissions summary.

According to these results, the most harmful method for the environment is the grey ammonia production method with a global warming potential of 127.1 gCO_2-eq./MJ of ammonia. The effect of the fuel used for feedstock overseas transportation on total emissions was negligible. With the implementation of the CCS system, CO_2 emissions were significantly reduced, but even with 90 % CO_2 capture rate, GHG emissions of blue ammonia did not come even close to the emission values of green ammonia.

The dominance analysis shown in Figure 35 illustrates where in the life cycle the largest GHG emissions occur. In the case of grey ammonia, ammonia production processes dominate the global warming impact. GHG emissions from raw material (LNG) production are also significant for both grey and blue ammonia. As already stated above, CCS significantly cuts the emissions from blue ammonia production. The analysis for green ammonia is markedly different, as greenhouse gas emissions are caused almost exclusively by end use.

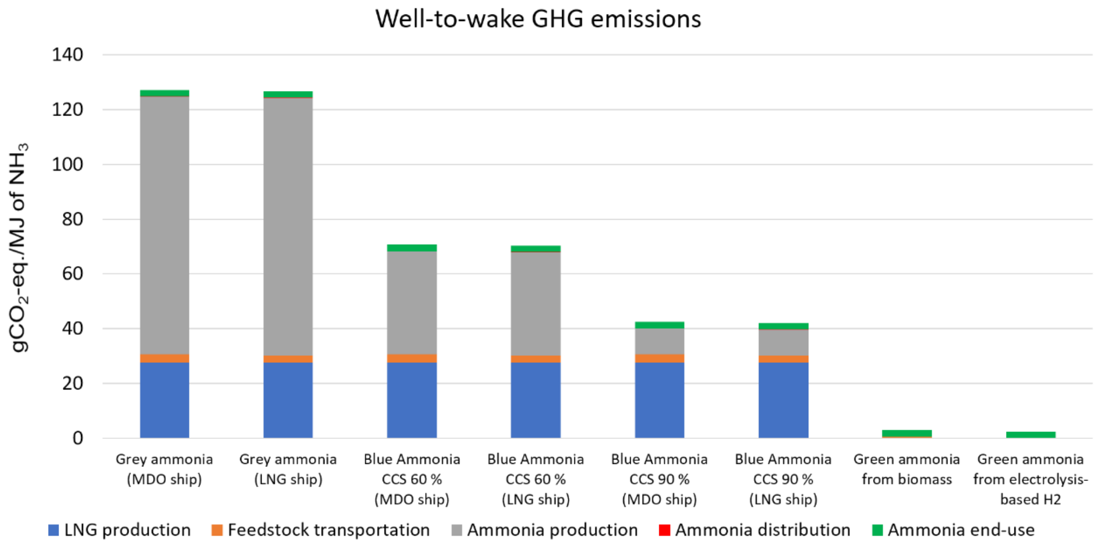


Figure 35. GHG emission divided into different phases of the life cycle.

Based on the findings of this thesis, it is clear that there is a huge need to reduce the use of fossil fuels in ammonia production. The use of sustainable biomasses and renewable energy-powered electrolysis-based hydrogen in ammonia production can significantly reduce the climate impacts of ammonia production.

9 Discussion

Four different ammonia production methods were defined and the life-cycle GHG calculation was made for chosen production pathways. In each production method, the Haber Bosch method was used for ammonia production. The feedstock and its delivery for each chosen method differed.

As a result of these calculations, green ammonia produced from electrolysis-based hydrogen causes the least amount of GHG emissions and is therefore the best option for environment and climate. The second-best ammonia production method for the environment and climate is green ammonia produced from biomass ammonia for the environment. Blue ammonia with 90 % CCS produces GHG emissions more than the green ammonia production methods studied here but less than grey ammonia production which is according to the calculations the worst option for environmental and climate reasons.

The most important factor effecting the difference between the green ammonia production pathways was the supply of feedstocks needed for biomass ammonia production. While evaluating biomass ammonia production in this study, forest products were used as feedstock in LCA calculations. To prevent the emission value from increasing, feedstocks are supplied over shorter distances in the biomass ammonia production method. However, the difference between the well-to-wake emissions for green ammonia options was relatively small, the well-to-wake emissions being 2.9 gCO_2-eq./MJ_{NH3} for green ammonia produced from biomass and 2.4 gCO_2-eq./MJ_{NH3} for green ammonia produced from electrolysis-based hydrogen.

The most important factor in the increase of CO_2 values is directly proportional to the variability of the carbon value contained in the feedstocks used in production. The feedstock required to produce blue and grey ammonia has a high CO_2 emission value.

By using CCS technology in the production of blue ammonia to reduce the emission value resulting from grey ammonia production, a significant reduction in the emission value resulting from production was observed.

The feedstocks to produce blue and grey ammonia was provided from the American state of Texas, and this supply was carried out through a ship operation. Two types of fuels, LNG and MDO, were determined to be used as fuel on the ship and emission calculations have been made between them. The emission value of LNG is lower than of MDO.

However, when ammonia is used as fuel in ship transportation, it can be preferred as an important fuel option. The emission value resulting from the use of ammonia as shipping fuel is lower than LNG and MDO. The use of renewable ammonia in shipping, instead of LNG or MDO can significantly reduce the environmental impact of shipping.

Considering the importance of ammonia production and its effects on LCA, it is important to increase the capacity of green and biomass ammonia production to reduce the amount of emissions formed in ammonia production. When fossil fuels are used, the blue ammonia production method is an important option in ammonia production compared to the production of grey ammonia.

The distance determined for the supply of raw material used in green, biomass based, ammonia was 120 km. Production feedstock of biomass ammonia was selected from forest products. The locations were determined between Lahti and Helsinki in this study. If shorter distances are determined for the supply of forest products in biomass ammonia, a significant win in reducing emission values can be achieved. Green ammonia is the cleanest ammonia production method for the environment. When the emission values for production are examined, the production model that has the least impact on the environment is the green ammonia production method.

The produced ammonia could be distributed and bunkered within a 100 km range to be used as fuel on the ship. Emissions generated during bunkering were not taken into account in this study because there is not enough initial data on ammonia bunkering.

10 Conclusions

The aim of this study was to examine the environmental impact of four different production methods of ammonia. They were blue, grey, green (via electrolysis) and green (biomass based) ammonia. The method for evaluating the impact of the production methods was LCA calculations which was conducted in line with the International Maritime Organization (IMO) LCA guidelines.

Based on the results, following conclusions can be made:

- Life-cycle greenhouse gas (GHG) emissions of gray ammonia span feedstock transportation, production, distribution, and end use, collectively contributing to high total emissions of 126.73–127.10 gCO_2-eq./MJ_{NH_3} depending on transportation methods. The elevated carbon footprint of gray ammonia makes it a less viable option in terms of environmental sustainability. The reliance on fossil fuels in its production and transportation processes amplifies its contribution to greenhouse gas emissions, highlighting the urgent need for more sustainable alternatives.

- With 60% CCS, a significant reduction in the carbon value is achieved in the production of blue ammonia, and with 90% CCS, the carbon emission value can be reduced more. At 60% CCS, emissions are reduced to 70.28 gCO_2-eq./MJ_{NH3}, nearly halving emissions compared to gray ammonia. Increasing the CCS rate to 90% further decreases emissions to 42.1 gCO_2-eq./MJ_{NH3}, showcasing the effectiveness of advanced CCS technologies. This approach bridges the gap between traditional gray ammonia and fully renewable green ammonia. While not entirely eliminating emissions, blue ammonia with CCS represents a transitional pathway toward a more sustainable industrial landscape. Advancements in CCS technologies are crucial for maximizing its potential until green ammonia solutions become widely feasible.

- The need to reduce the use of fossil fuels in ammonia production is huge. The use of sustainable biomasses and renewable energy-powered electrolysis-based hydrogen in ammonia production can significantly reduce the climate impacts of ammonia production. In conclusion, shifting to green ammonia production is essential for reducing the environmental impact of ammonia manufacturing and supporting global decarbonization goals. Among the different green ammonia production methods, biomass-based production proves to be highly sustainable, with emissions significantly lower than traditional methods. Its Well-to-Wake total of just 2.94 gCO_2-eq./MJ_{NH_3} makes it a promising alternative to fossil fuel-dependent processes.
- By utilizing renewable energy for hydrogen production and sustainable biomass as feedstock, this approach offers a practical solution for lower-carbon ammonia production. Adopting these low-emission technologies can help industries reduce their carbon footprint and contribute to long-term environmental sustainability.
- Electrolysis-based ammonia production expresses the effective integration of renewable energy and advanced industrial processes, showing its potential to significantly decarbonize ammonia production while enhancing environmental sustainability. By achieving a Well-to-Wake total of just 2.4 gCO_2-eq./MJ_{NH3}, it sets a new benchmark for sustainable practices in the chemical industry. As the world transitions to a low-carbon future, this method is poised to play an important role in decarbonizing ammonia production and contributing to global sustainability efforts. The Well-to-Wake total of 2.4 gCO_2-eq./MJ_{NH3} demonstrates the transformative potential of renewable energy in ammonia production. Compared to gray ammonia, which can exceed 127 gCO_2-eq./MJ_{NH3}, this method achieves an emission reduction of over 98%.

The analysis of ammonia production, from the supply of raw materials to its utilization as fuel, reveals significant insights into the environmental and operational implications of various production methods. Among these, the biomass-based ammonia production method stands out as the second-best alternative in terms of efficiency and sustainability. Additionally, this approach aligns with green production principles, offering a viable path toward reducing the environmental impact of ammonia production. Future efforts should focus on further optimizing biomass ammonia production to enhance its feasibility and adoption on a global scale.

The assessment of ammonia production through a life cycle perspective reveals that grey ammonia production has a considerably greater environmental impact compared to other production methods, as indicated by emission calculations. Among the four approaches analyzed, grey ammonia production stands out for its high emission levels and negative environmental consequences. To address this issue, expanding the capacity for green ammonia production emerges as a critical strategy. This shift toward green ammonia production has the potential to significantly reduce emissions and minimize the environmental footprint of ammonia production processes.

Based on the analysis and calculations carried out in this study, it is apparent that green production methods for ammonia should be prioritized. Additionally, further advancements and optimization of these sustainable techniques are necessary to enhance their efficiency and practicality, fostering the development of more sustainable ammonia production practices.

11 Summary

Ammonia is the most basic feedstock in fertilizer production. At the same time, it is aimed to be used in future internal combustion engines to reduce the use of fossil fuels. Many trials have been carried out in testing ammonia in engines and it is found to be a promising alternative fuel especially in marine industry. Ammonia has many different methods for production. Natural gas is the most important source to produce ammonia globally but in order to reduce the environmental impact of the production, green ammonia production methods are required. Life Cycle Assessment (LCA) is an important tool for examining potential environmental impacts from ammonia production.

Ammonia production methods and sources were studied in this study. LCA emission calculations were made for four different ammonia production. The aim of the calculations was to examine the environmental impact of four different production methods. The chosen and defined production pathways were fossil pathways, blue and grey ammonia, and green ammonia from electrolysis-based hydrogen and green ammonia from biomass.

The feedstock, natural gas, for grey and blue ammonia was supplied from Texas (USA) to Helsinki (Finland) by ship. Two different fuels, LNG and MDO were selected and compared for the ship operation. Biomass for green ammonia was forest residues which were carried out from Lahti to Helsinki and ammonia was produced in Helsinki. The Haber Bosch method was used for ammonia production. LCA calculations in line with IMO LCA guidance were made for each different ammonia production method.

According to these results, the most harmful method for the environment was the grey ammonia production method with a global warming potential of 127.1 gCO_2-eq./MJ of ammonia. The effect of the fuel used for feedstock overseas transportation on total emissions was negligible. With the implementation of the CCS system, CO_2 emissions were significantly reduced, but even with 90 % CO_2 capture rate, GHG emissions of blue ammonia did not come even close to the emission values of green ammonia.

In the case of grey ammonia, ammonia production processes dominate the global warming impact. GHG emissions from raw material (LNG) production are also significant for both grey and blue ammonia. As already stated above, CCS significantly cuts the emissions from blue ammonia production. The analysis for green ammonia is markedly different, as greenhouse gas emissions are caused almost exclusively by end use.

Based on the findings of this thesis, the use of fossil fuels in ammonia production must be cut down. The use of sustainable biomasses and renewable energy-powered electrolysis-based hydrogen in ammonia production can significantly reduce the climate impacts of ammonia production.

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