Ammonia Production Processes from Energy and Emissions Perspectives: A Technical Brief

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Understanding ammonia production

This document includes technical descriptions of main ammonia production technologies to understand current production pathways, associated energy usage, process emissions status and the potentials for sustainable ammonia production. It provides an accessible reference with key information and process data for the public, policy makers, and in particular modelers who needs to know the essential basics of ammonia production processes for process energy and material modeling/analysis

purposes. To this aim, this brief covers key aspects as below:

- Overview of the global/regional ammonia production including quantities, major production technologies and feedstocks
- Detailed description of the production technologies and involved unit processes
- Mass and energy analysis of each unit process
- Overall performance of commercial ammonia plants including energy and emission intensities from different production technologies
- Major low-carbon technologies for ammonia production including the details about technology status, performance, and production cost.

Overview of global ammonia production

Ammonia (NH_3) is one of the largest volume products in the chemical sector with a global production of approximately 185 million metric tons in 2020 (IEA, 2021a). In 2020, ammonia production was responsible for ~2% of total final energy consumption (8.6 EJ) and ~1.3% of total CO_2 emissions from the energy system (~450 million tons CO_2) (IEA, 2021a; X. Liu et al., 2020). Demands for ammonia are mainly related to agriculture, such that more than 80% of the ammonia produced worldwide is utilized for fertilizer manufacturing (mainly urea and ammonium salts). Other applications include the production of nitric acid (around 5%, used for making e.g., explosives), polyamides (around 5%, used for making e.g., textiles), and a variety of pharmaceuticals and cleaning products (Bazzanella et al., 2017). Ammonia is principally manufactured from hydrogen (H_2) and nitrogen (N_2), which are combined into ammonia through the Haber–Bosch process. Typical production capacities are 1000-1500 tons of ammonia per day (t/d) for large plants, while giant plants may have capacities of 2000-3000 t/d (European Fertilizer Manufacturers' Association (EFMA), 2000; Rossetti, 2020).

To produce ammonia, the needed reactants (H_2 and N_2) must first be synthesized. The required nitrogen is extracted from air using a process known as nitrogen fixation (Smith et al., 2020). There are multiple ways of producing hydrogen. Most commonly, hydrogen is obtained from different hydrocarbon feedstocks including natural gas, oil and coal, although alternative pathways from renewable feedstocks, e.g., biomass, are also possible and have received much attention recently (Demirhan et al., 2019). Hydrogen can also be produced using water and electricity through electrolysis as another alternative to using hydrocarbon feedstocks (Rossetti, 2020).

At hydrocarbon feedstock plants, the ammonia production process can be divided into three major stages, as shown in Figure 1 (IEA, 2013). The syngas production stage starts with producing synthesis gas (syngas)—which contains hydrogen, carbon monoxide and carbon dioxide—followed by carbon monoxide conversion to increase the hydrogen content of the syngas. Next, the syngas purification stage removes acid gas, mainly CO_2, to produce pure hydrogen. Finally, in the ammonia synthesis stage, the hydrogen is combined with nitrogen to produce ammonia.

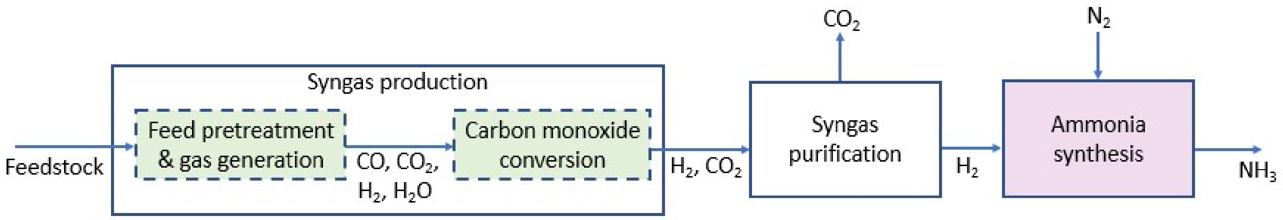

Figure 1. Main ammonia production steps

Currently there are three major industrial syngas processes: natural gas steam reforming, coal gasification, and partial oxidation/steam reforming of oil feedstocks such as naphtha, LPG and fuel oil. The availability of the feedstock and required process energy are the key factors in determining the technology for ammonia production. China as the largest ammonia producer (responsible for 29% of global ammonia production in 2019) produces its ammonia mainly via the coal gasification process, because of its abundant access to coal. Due to the availability of low-cost natural gas in United State, Middle East and Russia, natural gas steam reforming is the dominant production process in these regions. Figure 2 shows share of ammonia production from different world regions, and the syngas production processes implemented globally.

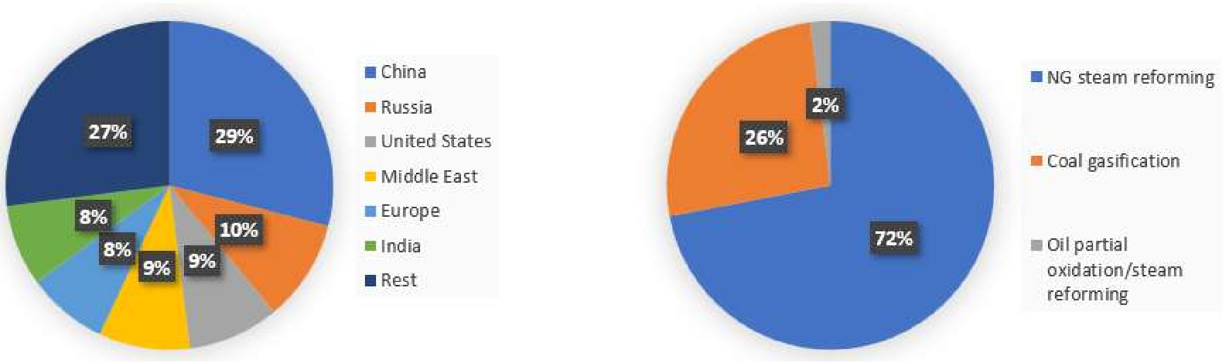

Figure 2. General view of global ammonia production (183 Mt/y in 2019) by (a) regions and (b) syngas production technologies (IEA, 2021a)

The ammonia industry has informally adopted a color scheme to describe the carbon intensity of different production methods (Figure 3). Brown and gray ammonia refers to ammonia produced from fossil fuel feedstocks (from coal and natural gas, respectively) which involves high levels of CO_2 emissions. Blue ammonia also refers to ammonia produced from fossil fuel feedstocks but associated with carbon capture and storage (CCS) technology to capture the generated CO_2 instead of releasing it to the atmosphere. Blue ammonia production is just ~1Mt/year based on existing CCS projects (located in US, Canada, and China), which can be increased to 4Mt/year by 2030 based on the announced projects. Green ammonia is produced using electrolysis powered by renewable electricity to produce H_2 instead of using hydrocarbon feedstocks, resulting in no CO_2 emissions. Current and announced electrolysis projects could bring the green ammonia production to more than 3Mt/year by 2030 (Bird et al., 2020; IEA, 2021a).

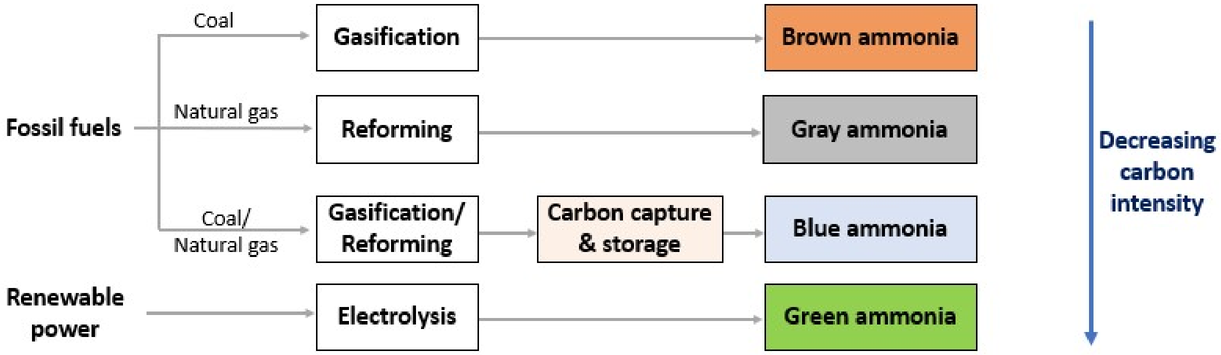

Figure 3. Categorizing ammonia production pathways based on the carbon intensity

Within the overall ammonia production process, the syngas production stage requires the most energy (60-70% of total energy consumption). The energy required for syngas production is also dependent on the feedstock employed; e.g., syngas production with solid feedstocks like coal has higher process energy intensity due to the additional energy required to operate equipment for pretreatment and processing the solid feedstock and its transformation to the required syngas (Hiller et al., 2006). Overall, natural gas steam reforming (which has the highest share of global production) has higher energy efficiency, lower CO_2 emissions (due to the higher amount of hydrogen produced per mole of consumed carbon), and generally lower costs compared to other syngas production technologies. Table 1 shows relative energy requirements and capital costs corresponding to different hydrocarbon feedstocks for an ammonia plant with 1800 t/d capacity (Appl, 2011) . Relative CO_2 emissions for different production routes are also presented in Table 1, among which the coal-based route has the highest CO_2 intensity (2.4 times higher than the natural gas-based route) (IEA, 2018; IFA, 2009). Specific energy and emissions intensities are presented later in this technical brief.

Table 1. Relative investment/energy requirement of different fossil fuel-based ammonia production routes

	Natural gas	Naphtha	Heavy fuel oil	Coal
Relative specific energy requirement (LHV)	1	1.1	1.3	1.6
Relative investment cost	1	1.15	1.5	2.5
Relative CO_2 intensity	1	1.53	1.88	2.38

Ammonia production process technologies

As mentioned, the ammonia production process generally involves syngas generation and purification steps, followed by the Haber-Bosch process for ammonia conversion. Depending on the feedstock type, different technologies are implemented for syngas generation and purification, while the ammonia synthesis stage can be considered identical for all. Typical process flowsheets representing the major ammonia production technologies are shown in Figures 4 and 5 for light and heavy hydrocarbons, respectively. Light hydrocarbons include natural gas and naphtha, whereas heavy hydrocarbons include fuel oil and coal. Key process details are described in the sections that follow.

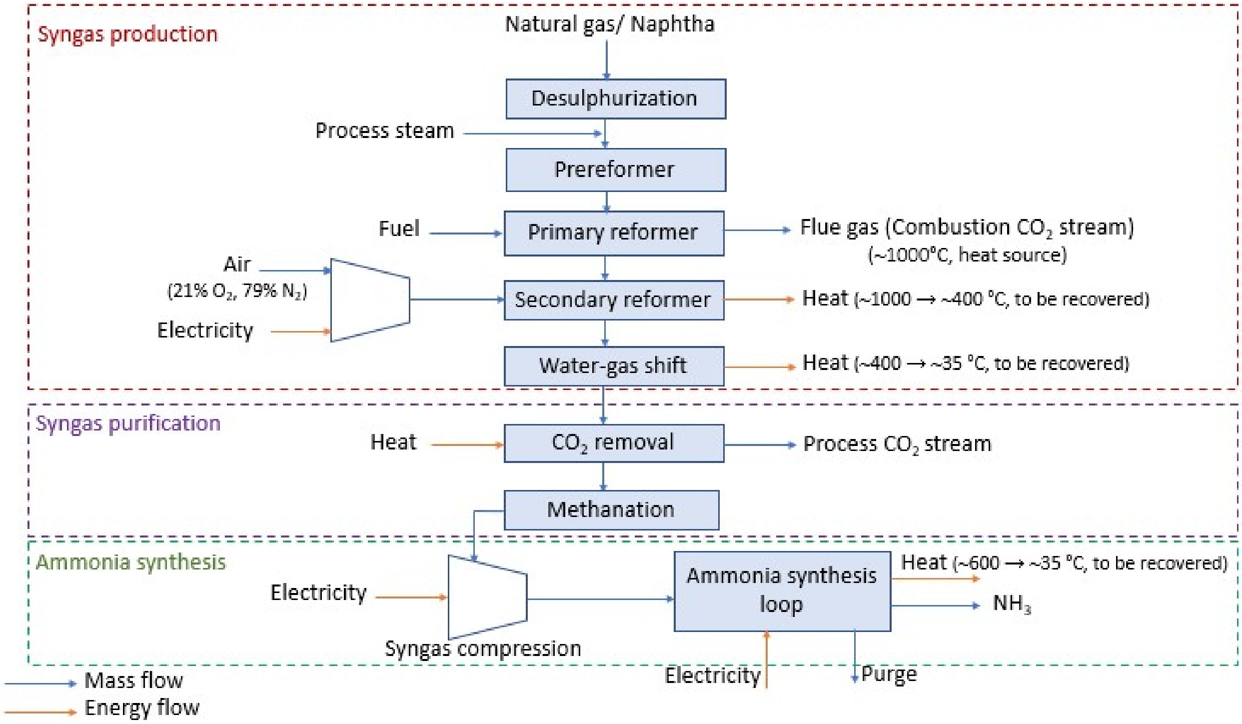

Figure 4. Typical process flowsheet for steam reforming of light hydrocarbons

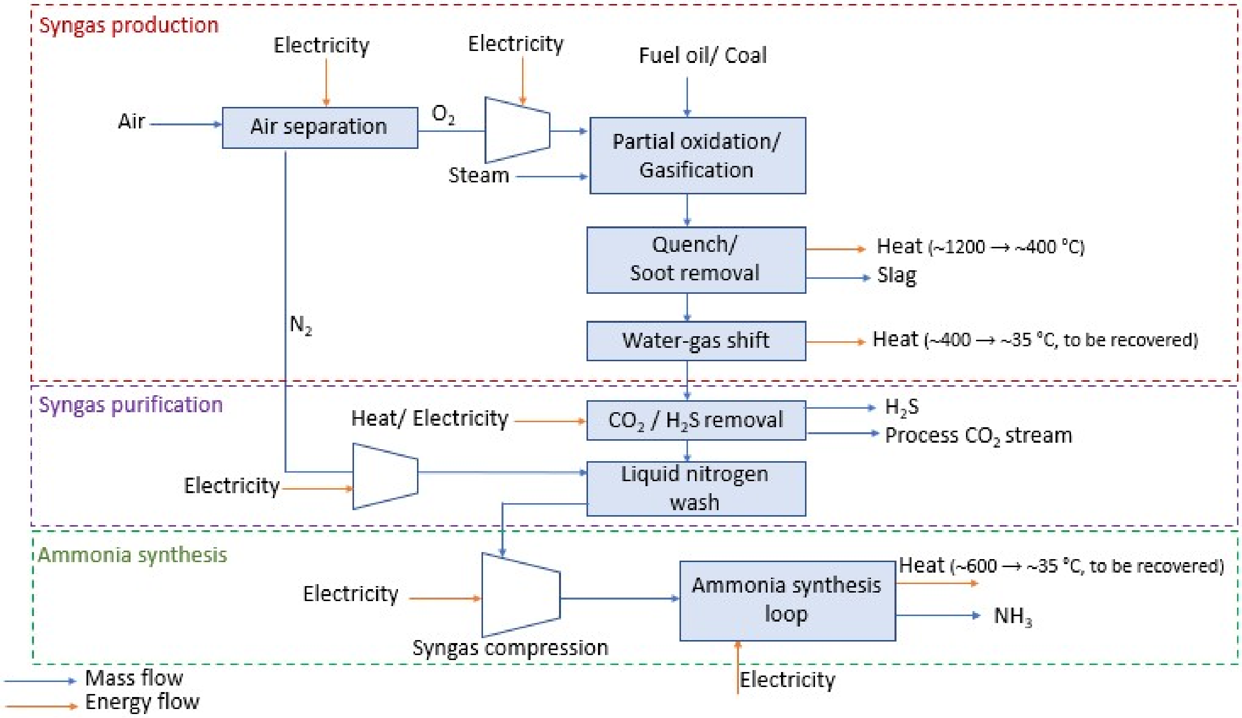

Figure 5. Typical process flowsheet for partial oxidation/gasification of heavy feedstocks

1. Steam reforming of light hydrocarbons

Steam reforming is the standard process for producing syngas from light hydrocarbons, which range from natural gas (methane) to naphtha (max C_{11}) (Appl, 2011). The light hydrocarbon feedstock is first passed through a desulfurization unit to remove any sulphur compounds that would otherwise contaminate catalysts used in the subsequent reforming process.

In the overall reforming process, the light hydrocarbon feed is mixed and reacts with steam over a catalyst according to the general reaction to produce syngas:

$$C_nH_{2n+2} + nH_2O \leftrightarrow nCO + (2n+1)H_2 \qquad (1)$$

The optimum steam to carbon molar ratio (mole H_2O to mole C in the feed) depends on several factors, including the feedstock composition, the reformer capacity, and the subsequent water-gas shift operating conditions. Although reduction of the steam to carbon ratio results in process energy savings, this ratio should not be lowered arbitrarily. Low ratios usually lead to carbon deposits on the catalyst (resulting in catalyst deactivation). Therefore, typically steam to carbon ratio of around 3 is used in modern commercial reformers (European Fertilizer Manufacturers' Association (EFMA), 2000).

Steam reforming of the feed usually starts in an adiabatic reactor that is called a pre-reformer and is located upstream of the main reformers (Hiller et al., 2006). The preheated mixture of feed and steam (500-600°C) enters the pre-reformer, in which the non-methane hydrocarbon fraction within the feed is completely converted to syngas. The syngas leaving the pre-reformer is then reheated (as the pre-reformer is slightly endothermic resulting in a temperature drop of ~60-70°C) and enters the main reforming reactors (primary and secondary reformers) for further conversion of the remaining methane fraction. The primary reformer consists of tubes filled with nickel-containing catalysts in a furnace box. The composition of the syngas leaving the primary reformer is based on the chemical equilibrium of following reactions:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^{\circ}_{298} = 206 \text{ kJ/mol} \qquad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol} \qquad (3)$$

As indicated by the above enthalpies of reaction (ΔH°_{298}), the overall reaction is strongly endothermic and requires additional heat (such that the gas temperature is increased from 500-600°C at the reformer's inlet to 780-830°C at the reformer's outlet). This additional is supplied by combusting fuels in the burners of the furnace box. The flue-gas leaving the burners is one of the main sources of air emissions from the plant containing mainly CO_2 and NO_x. Usually, the heat contained in the flue-gas (which has temperatures higher than 900°C) is recovered for use in process stream preheating and steam generating/superheating within the plant. The primary reformer's fuel energy requirement in the conventional process is 40-50% of the process feedstock energy content and typically ranges between 7.2 and 9.0 GJ (LHV) per ton of ammonia produced (European Fertilizer Manufacturers' Association (EFMA), 2000; Rafiqul et al., 2005). Accordingly, there are two separate CO_2 streams in ammonia plants: process CO_2 produced from stoichiometric conversion of the feedstock to hydrogen (concentrated CO_2 stream) and the combustion CO_2 in the flue-gas resulted from burning fuels (dilute CO_2 stream).

Up to 60% of the feedstock is converted to syngas in the primary reformer. To complete the remaining conversion, a higher temperature is required, which is achieved through a secondary reformer. In the secondary reformer, part of the feed is internally combusted with process air. The combustion provides the required heat for completing the endothermic reforming reaction and the air provides the nitrogen required for ammonia synthesis. The process air is first compressed to the reforming pressure (which accounts for about one third of the total electricity consumed in the plant) and preheated (Flórez-Orrego & de Oliveira Junior, 2016). It then reacts with the process gas over a nickel-based catalyst within the secondary reformer wherein up to 99% of the hydrocarbon feed is converted. The temperature of the exit syngas is around 1000°C. In general, the extent of conversion in each of the primary and secondary reformers can be adjusted and optimized for different commercial plants and process configurations. Conventionally, the degree of feedstock conversion in the primary reformer is usually adjusted such that the air stream to the secondary reformer supplies both the required heat and the stoichiometric nitrogen to hydrogen ratio (N_2/H_2=3) (Appl, 2011).

The typical operating pressure in the primary and secondary reformers is 25–35 bar. It should be noted that although the steam reforming reaction is thermodynamically favored at low pressure, the reforming pressure is usually selected as high as possible in order to minimize the pressure gap (ammonia synthesis is executed at > 100 bar) and thus the compression duty between the syngas production and ammonia synthesis units for reduced compression costs (Rossetti, 2020). The gas leaving the secondary reformer is then cooled to 350-400°C and its heat content usually is recovered in a waste heat steam boiler (to produce high pressure steam for use in turbines to generate electricity) before entering the water-gas shift reactors.

Besides the conventional approach of using a fired primary reformer and a secondary reforming with stoichiometric air input (stoichiometric N_2/H_2 ratio), some modern versions of the steam reforming process can be considered for new plants. These variants are mainly designed for reducing the load on the primary reformer and transferring some of the conversion duty to the secondary reformer as the primary reformer is usually identified as the bottleneck of the reforming process (Appl, 2011; Rafiqul et al., 2005).

One variant is steam reforming with decreased firing in the primary reformer and excess process air flow to the secondary reforming. The decreased heat supply to the primary reformer leads to lowered outlet temperature, increased firing efficiency as well as reduced size and cost of the primary reformer. Besides, the milder operating temperature prolong the catalyst lifetime. The reduced heat supply in the primary reformer necessitates an increased internal firing of the second reformer in order to achieve a same degree of total reforming (for which around 50% more process air input is required compared to the conventional process). Due to excess air input to the secondary reformer (over-stoichiometric N_2/H_2 ratio), further adjustments of the syngas composition are usually required upstream of the ammonia synthesis section.

Another variant which avoids a fired primary reformer is heat exchange autothermal reforming. For this technology, the high-level heat content of the outlet gas from the secondary reformer is recycled to the process itself and used in the primary reformer (a heat exchange reformer) instead of being used for steam generation and therefore eliminates the fired furnace. This means emissions to the atmosphere are reduced significantly in this variant due to flue-gas elimination from the primary reformer. Usually oxygen-enriched air or excess air is required in the secondary reformer to address the heat balance between the exchanger reformer and secondary reformer (European Fertilizer Manufacturers' Association (EFMA), 2000; Hiller et al., 2006).

2. Partial oxidation/ Gasification of heavy fuel oil and coal

The catalytic steam reforming technology described in the previous section can be implemented only for light hydrocarbons; it is not suitable for heavy hydrocarbons such as fuel oil. Heavy hydrocarbons typically contain a substantial amount of sulfur which contaminates the reforming catalyst. Additionally, carbon deposition occurs on the catalyst due to the cracking reactions, which blocks the catalyst pores and limits inter-particle flow. Therefore, for heavy fuel oil and coal the only choice is the non-catalytic partial oxidation/gasification technology, which is however applicable for treating any type of hydrocarbon feedstock (Appl, 2011). The process involves reacting dry or slurried feedstock with steam and oxygen in a gasifier at high temperature and pressure.

The following simplified reaction patterns exist in the gasifier in which fuel oil or coal reacts with an amount of oxygen insufficient for full combustion to CO_2:

$$C_nH_m + n/2O_2 \rightarrow nCO + m/2H_2 \qquad (4)$$

$$C + 1/2O_2 \rightarrow CO \qquad \Delta H^{\circ}_{298} = -111 \text{ kJ/mol} \qquad (5)$$

Besides oxygen, a small amount of steam is usually added leading to the following reactions in parallel:

$$C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2 \qquad (6)$$

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H^{\circ}_{298} = +131 \text{ kJ/mol} \qquad (7)$$

Some CO_2 and soot are formed in addition, as well as hydrogen sulfide gas (H_2S) (from the sulphur compounds in the feed). The overall gasification reaction is exothermic such that no additional heat supply is required. The gasifier operates between 1200 and 1400°C and at higher pressure compared to steam reforming (as high as 80 bar). An air separation unit (ASU) is required for supplying oxygen for the partial oxidation process. Cryogenic ASUs are currently the most efficient technology in use to supply high purity oxygen in large quantities (Jiang & Feng, 2019). The ASU includes several parts for compression, purification, and separation of air into its principal components and typically requires power consumption of 245 kWh/t produced oxygen for its operation (Gerhard, 2009). The produced O_2 and N_2 then needs to be compressed to the pressure of the section they are used in.

The main examples of the partial oxidation/gasification process are the Texaco and Shell processes (Preciado et al., 2012; Rossetti, 2020). For coal as the feedstock in particular, Texaco coal water-slurry gasification is the leader commercially worldwide due to its mature and simple technology suitable for almost all kinds of coal including lignite, bituminous and anthracite (Zheng & Furinsky, 2005). In the Texaco process, a coal-water slurry (containing 60 to 70% coal) and an oxygen stream from the ASU are fed to the gasifier in which coal reacts exothermally with oxygen at high pressure (>70bar) and temperature (>1200 °C) to produce syngas and slag. The mixture leaving the gasifier is quenched with water such that the slag is solidified and a cooled water-saturated syngas free of carbon particles and contaminants is produced and leaves at a temperature between 200 and 300°C. The solidified slag is removed from the gasifier and mainly treated by stacking and being disposed in landfills (Hoffman, 2005; K. Liu et al., 2009).

3. CO removal

The resulting gas from the steam reforming and partial oxidation/gasification processes is mainly composed of H_2, CO and CO_2. To increase the hydrogen concentration required for ammonia synthesis, most of the CO further reacts with steam in water-gas shift reactors as according to the following reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol} \qquad (8)$$

The above exothermic reaction is favored at low temperature for improved CO conversion. To this aim, the heat of reaction should be removed in appropriate way (to keep the temperature low), while suitable catalysts must be implemented to achieve a sufficient reaction rate. Based on that, the process is typically performed in steps via two catalytic reactors (a high temperature shift reactor, HTS, followed by the low temperature one, LTS) with intermediate heat removal between them. The heat removed during gas cooling between the HTS and LTS reactors is usually recovered for producing high pressure steam for use in other processes.

In the steam reforming process, the gas from the secondary reformer (which contains 12-15% mole CO in dry basis) reacts with steam in the HTS reactor through a bed of iron-chromium oxide catalyst at around 400°C, which results in a residual CO content of about 3%. The gas from the HTS is then cooled and enters the LTS, which is filled with a copper-zinc oxide catalyst that operates at about 200-250°C and results in residual CO content of 0.1–0.3%. Compared to steam reforming, the syngas from partial oxidation/gasification has up to 50% higher CO content and higher amounts of sulfur compounds (mainly H_2S). The sulfur compounds can be removed prior to the water-gas shift or can be removed afterward, when a sulfur-tolerant catalyst (typically cobalt-molybdenum-alumina catalyst) is used handle the sulfur containing syngas (Appl, 2011; European Fertilizer Manufacturers' Association (EFMA), 2000).

4. Process CO_2 removal

In addition to H_2 (and N_2 in the case of steam reforming), the syngas leaving the CO conversion shift contains CO_2, H_2S (present in syngas from partial oxidation/gasification), residual CO and excess process steam. These components must be removed as they add no value and are also poisonous for the subsequent ammonia synthesis catalyst. The gas is first cooled such that most of the excess steam is condensed. The heat removed during cooling can be used for other plant heating purposes, such as boiler feed water preheating. The CO_2 is then removed in a chemical or a physical absorption process. Chemical solvents are more effective at low CO_2 partial pressures (4-7 bar, applicable usually for syngas from steam reforming), while physical solvents have higher loading capacity at higher partial pressures (10-30 bar, mainly for the syngas produced from partial oxidation). In terms of energy consumption, chemical solvent-based processes are more energy intensive compared to physical-based processes mainly due to the high amount of heat required for solvent regeneration (Hiller et al., 2006).

Solvents for chemical absorption processes are typically aqueous amine solutions (e.g., MEA), tertiary amines solution (e.g., aMDEA), or hot potassium carbonate solutions. The MEA process is implemented widely and has a high regeneration energy consumption with ~3-4 MJ/kg-CO_2 captured (Luis, 2016; Van Straelen & Geuzebroek, 2011), while for new plants more efficient processes (e.g., 2-stage aMDEA) are implemented with a heat consumption of 0.7-1.4 MJ/kg-CO_2 captured (European Fertilizer Manufacturers' Association (EFMA), 2000). Considering the process CO_2 (from feedstock conversion) in steam reforming of natural gas which is ~1.2 t-CO_2/t-NH_3, an energy consumption of 3.6-4.8 MJ/kg-NH_3 can be estimated for MEA-based CO_2 removal. This value can be reduced to ~0.8 MJ/kg-NH_3 with more efficient CO_2 removal solvents (Appl, 2011).

Main examples of physical absorption processes are the Selexol (glycol dimethylethers-based) and Rectisol (methanol-based) processes. The Rectisol process is the most widely used which employs methanol as the solvent (at a temperature of about -70 to -30 °C) to clean up the syngas by eliminating its CO_2 content as well as a deep H_2S removal (in particular, applicable for partial oxidation/gasification-based syngas). The Rectisol process has a specific power consumption of around 0.14 MJ/kg-CO_2 captured and specific heating consumption of 0.35 MJ/kg-CO_2 captured (Padurean et al., 2012). Compared to other physical absorption processes, it has relatively high operating and capital costs (e.g., the equipment costs of two times higher than the Selexol process), due to its complex configuration and the need for refrigerating the solvent (X. Liu et al., 2020; Preciado et al., 2012). Considering process CO_2 production in partial oxidation/gasification of heavy oils and coal, which is within the range of 2-3 t-CO_2/t-NH_3 (depending on feedstock's carbon to hydrogen ratio), a specific power consumption of 0.3-0.4 MJ/kg-NH_3 and a specific heating consumption of 0.7-1.1 MJ/kg-NH_3 to remove the stoichiometric CO_2 are associated with the Rectisol process.

Ammonia plants are often integrated with other plants, most commonly with urea plants which use the produced CO_2 as a feedstock. Globally, around half of the process CO_2 generated during ammonia production is implemented as the urea production input, with other applications in e.g., methanol production and beverage industry. In contrast to the process CO_2, it is not easy to capture the more dilute (and thus more expensive to separate) combustion-related CO_2 (in flue-gas) produced in ammonia plants and it is mainly released to the atmosphere (IEA, 2021a; Luis, 2016).

The purified syngas leaving the CO_2 removal unit has a residual CO_2 content of 100-1000ppm, based on the type and design of the removing unit.

5. Final purification

After the bulk removal of the CO and CO_2 through shift reaction and CO_2 removal units, the small amounts of these compounds remaining in the syngas need to be still removed as they can poison the ammonia synthesis catalyst. Commercial technologies for final gas purification include Methanation, Liquid Nitrogen Wash, Pressure Swing Adsorption, etc. Choices of different technologies depends on many factors, including the type of technology employed for syngas production, the energy consumption and availability of the purification technologies (Hiller et al., 2006).

Methanation is one of the common purification steps (the most used, in particular in steam reforming technology), which operates at 250-350°C on a nickel-based catalyst removing CO and CO_2 content to below 10 ppm by their conversion to CH_4 (inert gas). Another efficient way is implementing a Liquid nitrogen wash unit (operating at -180°C) which is mainly suitable for purifying syngas from partial oxidation/gasification technology. The nitrogen from ASU is compressed to the pressure of syngas production/purification units and then added into the liquid nitrogen wash column to remove all impurities from the syngas and to get the required N_2/H_2 ratio for ammonia synthesis (European Commission, 2007).

6. Synthesis gas compression and ammonia synthesis

The ammonia synthesis stage is comprised of units for syngas compression to high pressures, syngas conversion to ammonia, and, finally, ammonia separation. The latter two processes are depicted as the "Ammonia synthesis loop" in Figures 4 and 5.

During syngas compression, the purified syngas (containing H_2 and N_2) is compressed to the high pressures (100-250 bar) required for the ammonia synthesis reactors. As such, syngas compression is one of the main energy consumers (and thus operating cost items) in the whole plant. The converter (ammonia synthesis reactor) is the core of the synthesis loop in which the production of ammonia occurs on iron-based catalysts at the aforementioned pressures (100-250 bar) and temperatures of 350-550°C (the upper limit for catalyst resistance) as follows:

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \qquad \Delta H^{\circ}_{298} = -46 \text{ kJ/mol-NH}_3 \qquad (9)$$

The conversion from H_2 and N_2 to ammonia is generally only 20-30% per pass through the converter. The converted fraction is then separated from the unconverted fraction through the gas cooling unit, which leads to ammonia condensation. The unconverted gas is then mixed with fresh syngas and recycled to the synthesis converter. To control concentrations of any inert gases (mainly CH_4 and Ar) present within the synthesis loop, a small purge gas stream may need to be withdrawn continuously depending on the levels of inert gases within the syngas. There are different configurations of the ammonia synthesis loop with respect to the points of ammonia separation and fresh (make-up) syngas addition. The best arrangement from a minimum energy point of view is to add the fresh syngas after ammonia condensation/separation and before the converter, which results in the lowest ammonia content entering the converter, and the highest ammonia content for condensation (as shown in Figure 6). The purge should be withdrawn after separating ammonia and before introducing the fresh syngas. The purge gas is then scrubbed with water in order to recover ammonia before being used as fuel (e.g., for the reformer) or being sent for hydrogen recovery (Appl, 2011).

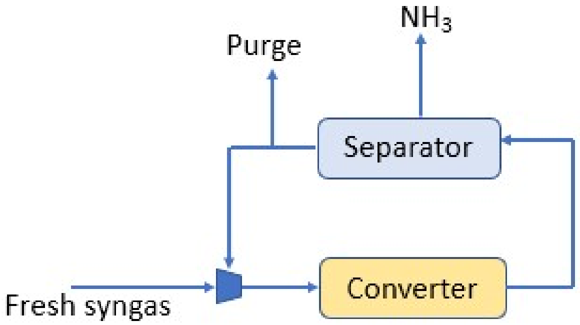

Figure 6. Typical ammonia synthesis loop configuration

Usually the ammonia condensation/separation cannot be achieved sufficiently using cooling water or air (depending on the loop pressure); therefore, a refrigeration system producing coolants with temperatures down to -25 °C is required to complete the ammonia condensation. It should be noted that increased synthesis loop pressure increases ammonia conversion due to the higher reaction rate and more favorable chemical equilibrium. Higher pressure also implies that cooling water (~ 25 °C) suffices for a satisfactory ammonia condensation, with no need for a refrigeration unit. However, a higher loop pressure means a higher power consumption for the compression stage, and usually economic optimizations are required to find the optimum operating conditions (European Commission, 2007). When cooling water can be used, its outlet temperature is around 40°C. This temperature is generally unattractive for in-plant heat recovery, so warm cooling water generally leaves the system without being recovered (typically rejected to the environment) (Flórez-Orrego & de Oliveira Junior, 2016).

Generally, in the ammonia synthesis loop there is no need for an external heat source because the ammonia synthesis reaction is exothermic. The produced heat from the reaction is a high-valued source which can be recovered to satisfy the temperature requirements of the converter feed-stream and to generate high pressure steam for use in other plant processes. In modern plants, the compressors of the synthesis loop (the syngas/recycle compressors as well as the ammonia refrigeration compressor) are usually centrifugal ones driven by steam turbines which work with the produced steam from the recovered waste heat available within the plant (European Fertilizer Manufacturers' Association (EFMA), 2000). Overall, electricity consumption values of ~0.32 to ~0.64 kWh/kg-NH_3 have been reported in literature for the synthesis loop, depending on the variations in the syngas production pressure, synthesis loop pressure and compression efficiencies (X. Liu et al., 2020).

Overall performance of commercial ammonia plants

In steam reforming-based ammonia plants based on light hydrocarbons, large quantities of waste heat are generated in the reforming, shift conversion, and ammonia synthesis processes. This waste heat is generally recovered for use in steam production and supplying different heat duties within the plant (e.g., for solvent regeneration in CO_2 removal system). Usually, enough high pressure (HP) steam (~100 bar) can be produced from waste heat to be used first in steam turbines for supplying the required electrical energy for the plant's compressors, pumps and blowers. After electricity generation, the turbine outlet steam is extracted at medium pressure (MP) at ~25-35 bar for use in the primary reformer (as the process steam) and for use in a secondary turbine for additional electricity generation. The steam exiting the secondary turbine is generally of low pressure (LP) suitable for use in low-pressure steam processes, such as the CO_2 removal unit. The surplus LP steam can also be exported e.g., to adjacent urea plants. A simplified view of a typical steam system in a steam reforming process plant is shown in Figure 7.

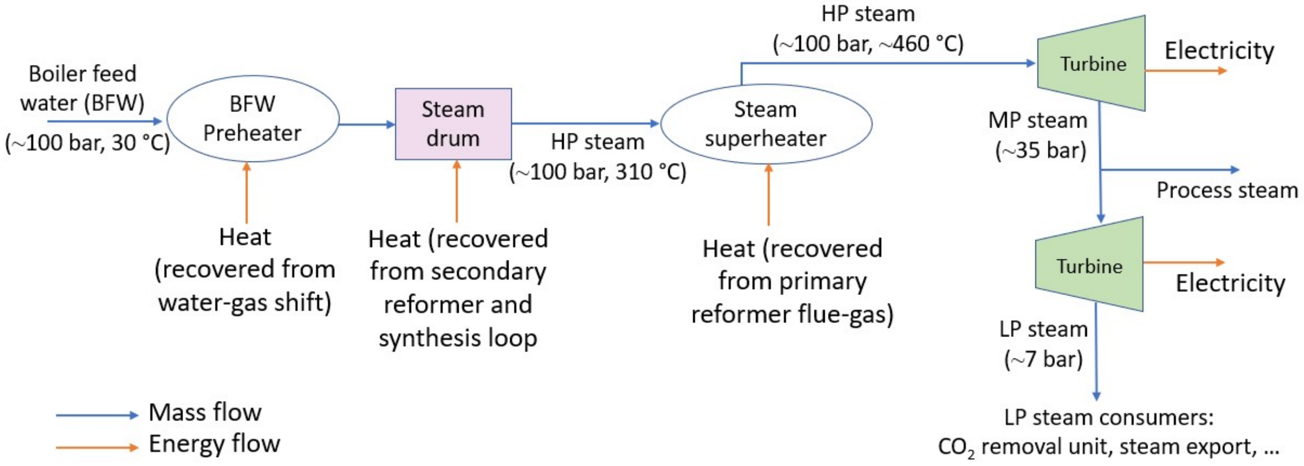

Figure 7. Typical steam system flowsheet of the steam reforming process

However, in partial oxidation/gasification plants based on heavy hydrocarbons, the level of waste heat recovery is usually lower than the steam reforming plants due to the absence of a fired primary reformer and the high-temperature flue-gas it generates. Therefore, low waste heat is available to be recovered and separate auxiliary boilers are usually required to provide steam for steam-driven compressors in partial oxidation/gasification plants

The energy consumption per unit of ammonia is nowadays 30% less than its value four decades ago thanks to process intensification efforts which involves substantial energy recovery, integration between different plant sections, and optimization of process operating conditions. Improvements are mainly accomplished through the increased energy recovery and heat exchange of process flows (e.g., using pinch analysis and heat exchanger network optimization), as well as increasing the process efficiency by identifying the main process energy losses due to irreversibilities (e.g., using exergy analysis). Besides, technology developments like the introduction of large centrifugal compressors, catalyst improvements (e.g., for shift conversion and ammonia synthesis), and CO_2 removal with new solvents are other contributors to the reduced energy needs of today's ammonia plants (Rossetti, 2020; Smith et al., 2020). Despite these historical efficiency improvements, further reduction of global energy consumption and CO_2 emissions in the ammonia industry still requires shifting production from inefficient plants to new production sites with best available technologies (BAT)[1] worldwide, which can reduce the energy consumption by 20-25% and greenhouse gas emissions by 30% compared to inefficient plants (IEA, 2021a; IFA, 2009). Table 2 represents the overall energy consumption and CO_2 emissions for Best available technology processes for ammonia production based on different feedstock and technology types (IFA, 2009).

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[1] Best available technology (BAT) and best practice technology (BPT) are references to the most advanced technologies in chemical and petrochemical industry. BPT addresses advanced technologies which are currently in use at industrial scale, while BAT refers to those which are not yet deployed commercially for industrial scale implementations.

Table 2. Total energy and emission comparison of BAT processes for ammonia production

Feedstock	Technology	Energy consumption GJ/t-NH_3	CO_2 emission t/t-NH_3
Natural gas	Steam reforming	28	1.6
Naphtha	Steam reforming	35	2.5
Heavy fuel oil	Partial oxidation/gasification	38	3
Coal	Partial oxidation/gasificaion	42	3.8

The type of feedstock and the implemented process technologies are the main factors affecting the levels of energy consumption and CO_2 emissions in ammonia production. Generally, the final energy use for oil-based ammonia production is roughly 30% higher compared to natural gas-based ammonia production, while final energy consumption of coal-based ammonia production is assumed to be around 50% higher than the natural gas-based process (IFA, 2009). Compared to BAT values, Table 3 summarizes the energy consumption in ammonia production plants working based on the best practice technologies, BPT (as the best technologies which are currently in use at industrial scale) and also the global average values as of 2017 by feedstock and onsite fuel (IEA, 2018, 2021). The energy intensity is broken down according to the onsite fuel combustion, grid electricity requirement and the excess steam generated.

Table 3. BPT and average energy and emission intensities for different ammonia production processes

Feedstock	Technology	Feedstock* GJ/t-NH_3	BPT GJ/t-NH_3			Average GJ/t-NH_3			Ave. CO_2 emission t/t-NH_3
			Fuel	Steam**	Elec.	Fuel	Steam	Elec.	
Natural gas	Steam reforming	20.7	13.5	-4.8	0.3	26.3	-9.3	0.3	2.1
Oil	Partial oxidation/ Gasification	20.7	20.5	-6.3	2	27.9	-8.4	2	3.3
Coal	Partial oxidation/ Gasificaion	20.7	19.6	-1.3	3.7	23.6	-1.5	3.7	4.6

* The share of feedstock energy use is usually approximated using the average of lower and higher heating value of the ammonia produced, as 20.7 GJ/t-NH_3 which is considered constant between different process routes (Saygin et al., 2011). ** Negative values represent generation of excess steam

Table 3 also includes the amount of CO_2 emissions for each production route; on average natural gas steam reforming has the lowest emissions intensity of 2.1 t-CO_2/t-NH_3, while in partial oxidation/gasification of fuel oil and coal, it is substantially higher, at about 3.3 t-CO_2/t-NH_3 and 4.6 t-CO_2/t-NH_3, respectively. The CO_2 emissions include process CO_2 (according to feedstock stoichiometric conversion, which is removed during CO_2 removal) and the CO_2 in the combustion gases (as part of flue-gases). On average, about one-third of the CO_2 emissions generated in natural gas-based production comes from fuel burning and two-thirds from using natural gas as a feedstock, while in the coal-based route, 25% of CO_2 emissions comes from fuel combustion and 75% from using coal as a feedstock (IEA, 2021a; Zhou et al., 2010).

Generally, when natural gas is available, natural gas steam reforming technology is the most efficient fossil fuel-based route for ammonia production. For a better perspective, disaggregated energy use data based on different unit processes for natural gas steam reforming process is also provided in Table 4 (Worrell et al., 2009). One can notice that most of the plant's fuel input is consumed in the primary reformer and the remaining in auxiliary boilers. The available heat from the waste heat boilers, ammonia synthesis loop, and the auxiliary boilers is implemented in the turbines/compressors, the primary reformer and CO_2 removal unit.

Table 4. Breakdown of energy use for a typical natural gas-based ammonia plant

Technology	Natural gas GJ/t-NH_3	Heat input/output GJ/t-NH_3
Primary reformer feed	20.4 – 22.3	
Primary reformer fuel	7.2 – 9	3 – 4.5
Waste heat boiler		-5 – -6
Shift and CO_2 removal		0.8 –1.2
Synthesis loop		-2.5 – -3
Auxiliary boiler	0.3 – 3.5	-0.2 – -3
Turbines/compressors		3.9 – 6.3
Others (e.g., flare)	0.2 – 0.7	
Total	28.1 – 35.5	0

*Negative values represent net steam generation

Low-carbon technology pathways for ammonia production

1. Energy efficiency improvement

Considering the long lifetimes of typically 20-50 years or more for ammonia plants, specific attention is needed on improving the energy efficiency of the existing facilities by upgrading and retrofitting equipment with technologies such as waste heat recovery and improved process operations (IEA, 2021a). Steam is used throughout the ammonia production process for heating and steam reforming. As mentioned above in the overall ammonia plant performance, options for the improvement in energy efficiency mainly include increasing energy recovery and heat exchange of process flows, as well as increasing the process efficiency by identifying the main process energy losses due to irreversibilities. Besides, levers of large centrifugal compressor implementation, catalyst improvements, and CO_2 removal with new solvents are other contributors to the reduced energy needs of today's ammonia plants (Rossetti, 2020; Smith et al., 2020).

2. Water electrolysis

Besides the fossil-fuel based pathways currently in use, ammonia can also be synthesized using renewable electricity and water electrolysis to produce syngas for the Haber-Bosch process. A typical process flowsheet is shown in Figure 8. Basically, an air separation unit is needed to supply the required nitrogen, while hydrogen is provided by water electrolysis. Among available technologies, Alkaline electrolysis technology is the most mature commercially in which an alkaline solution is used where ions in the water can conduct the current and thus electrolysis can happen (IEA, 2021a). Depending on the electrolysis technology, usually a hydrogen purification step after electrolysis should be considered. As in the conventional pathways, compressors are required for compressing H_2 and N_2 to the pressure of the ammonia synthesis convertors as well as for ammonia refrigeration/separation.

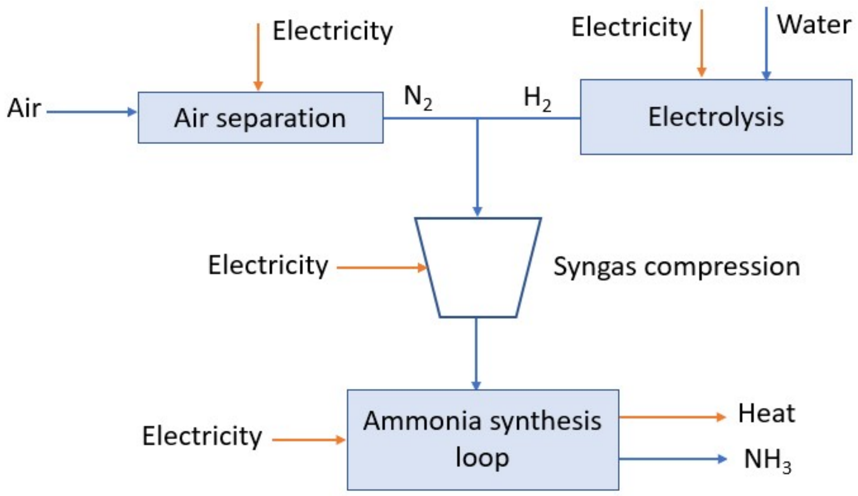

Figure 8. Water electrolysis-based ammonia synthesis

This route produces ammonia with zero direct CO_2 emissions given it is fueled entirely by electricity. Electrolyzers usually require about 53 kWh/kg-H_2 (corresponding to 188 GJ/t-H_2). As typically a ratio of 0.18 t-H_2/t-NH_3 is required for ammonia production, an electricity usage of 33.4 GJ/t-NH_3 is required for the hydrogen supply by water electrolysis. Accordingly, a total energy demand of 37.3 GJ/t-NH_3 can be calculated considering the power required for water electrolysis, compressors, and the ASU. Table 5 shows the electricity consumption of the main process steps of this production route (IEA, 2013). A recent IEA's report estimated a BAT value of 34.4 GJ/t-NH_3 for water electrolysis-based ammonia production, in which ~95% of the electricity is used for hydrogen production and the remaining 5% for the air separation and Haber-Bosch synthesis units (IEA, 2021a).

Table 5. Breakdown of the electricity use for water electrolysis-based ammonia production

	H_2 production	Compression	N_2 from ASU	NH_3 synthesis	Total
Electricity (GJ/t-NH_3)	33.43	2.14	0.41	1.35	37.3

The total production costs of renewable ammonia strongly depend on the price of low-carbon electricity and the investment cost of electrolyzer. Electrolysis-based ammonia production can compete with natural gas reforming route when electricity prices are low, natural gas prices are high and electrolyzer costs low (even in a low electrolyzer costs scenario, an electricity price of 40 USD/MWh or lower is needed to make electrolysis competitive). It has been reported that for water electrolysis-based technology, the cost ratio of the low carbon electrolysis-based ammonia to the natural gas-based one can change between 1.7 to 5.3 depending on the low-carbon electricity price (considered from 10 to 50 €/MWh) (Bazzanella et al., 2017). Therefore, in regions where are expected to have high natural gas prices and renewable electricity availability in the future (e.g. parts of Europe, China, Korea, Japan, and parts of Latin America) electrolysis can be a promising option for implementation of low carbon technologies in ammonia production (IEA, 2021a).

3. Bio-based ammonia synthesis

Lignocellulosic biomass has been considered as a sustainable hydrocarbon feedstock for ammonia production and the gasification route has been designed, analyzed, and implemented at pilot scale (Gençer et al., 2020). The biomass to ammonia production process is similar to the coal gasification process shown in Figure 4. Sánchez et al. (Sánchez et al., 2019) evaluated the CO_2 emission for biomass-based ammonia production produced by alternative gasification processes with a range of 0.7 kg-1.5 CO_2/kg NH_3 (carbon dioxide emission from biogenic carbon in biomass is neglected; only CO_2 emissions related to the electricity consumption). Gencer et al. (2020) indicated that the energy intensity of ammonia production is around 46.4 GJ/t NH_3 when biomass supplies both H_2 and electricity requirements of the process from the waste heat recovery. However, the economic prospects for ammonia production from lignocellulosic biomass from crop residues and energy crops (e.g., switchgrass) in the developed countries are currently unfavorable due to the low cost of natural gas (Gençer et al., 2020).

4. Electrochemical route of ammonia synthesis

Ammonia is currently produced predominantly via methane-fed Haber–Bosch process, which is a thermochemical process that operates at high temperatures (350–550 °C) and pressures (100–250 bar) Alternatively to the Haber-Bosch process, ammonia can be synthesized by electrochemical methods that have been proposed to have some advantages over traditional thermochemical methods (Lazouski et al., 2020). Electrochemical methods enable bond-formation steps using electricity, which offers an alternative driving force, voltage, that can enable operation at low temperatures and pressures (Schiffer & Manthiram, 2017). In addition, electrochemical cells often result in natural product separation due to the use of a membrane that keeps products generated at the cathode and anode separate (Schiffer & Manthiram, 2017). Figure 9 shows the overall configuration of electrochemical NH_3 synthesis. Here on the cathode, hydrogen in the form of H^+ and e^- reduces N_2 stepwise to NH_3. Water splitting-derived hydrogen is coupled at the anode to have overall ammonia production from N_2 and H_2O.

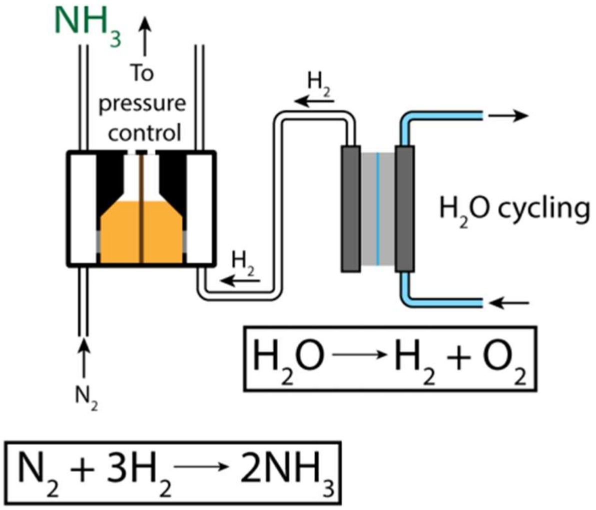

Figure 9. Electrochemical ammonia synthesis coupling with water electrolysis (Schiffer & Manthiram, 2017)

Instead of first splitting water to generate hydrogen and then reacting this hydrogen with nitrogen in a separate electrochemical reactor, it is appealing to react nitrogen and water directly in a single reactor:

$$2N_2 + 6H_2 \leftrightarrow 4NH_3 + 3O_2 \qquad (10)$$

Thermochemically, the reaction of water and nitrogen is not feasible at mild conditions. However, when a voltage of greater than 1.17 V is applied at ambient temperature and pressure, ammonia is thermodynamically favored compared to nitrogen and water (Schiffer & Manthiram, 2017). If run on renewable electricity, the CO_2 emissions of this route are minimal. However, the TRL of this advanced approach is low as 1-3 due to its significant difficulties with selectivity and throughput (Smith et al., 2020).

5. Carbon capture and utilization

High purity CO_2 streams are produced in the natural gas-based ammonia production process at the CO2 removal unit. Traditionally the CO_2 is removed using chemical based solvent absorption techniques (Zakkour & Cook, 2010). The removed CO_2 can be captured and used to synthesize other chemicals. The International Fertilizer Association (IFA) reports that the ammonia industry has already utilized around 36% of the CO_2 captured at the CO_2 removal unit for subsequent chemical production. Around 33% is currently used for the synthesis of ammonia into urea and the remaining 2.2% is sold on to other uses, such as CO_2 use for enhanced oil recovery (Zakkour & Cook, 2010).

Performance and cost

Table 6 summarizes statistics related to energy use, CO_2 emissions, and the current levelized costs of the aforementioned low-carbon technologies for ammonia production. Using hydrogen produced from water electrolysis for ammonia synthesis can have a considerable reduction in carbon emissions due to the utilization of renewable electricity. However, the levelized production cost for this technology is much higher compared to the cost of natural gas-based ammonia production (\$41-53/t-NH_3). In addition, the electrochemical methods of ammonia synthesis are still in the early stage and experimental or small-scale data indicate this route has higher energy intensity for ammonia production. CCS/CCU is available for decarbonizing the ammonia industry, but still needs additional investment for retrofitting existing ammonia plants. Since 2010, around \$15 billion in capital has been invested in the 15 large-scale CCUS projects in global (IEA, 2020a). The cost of CCS for concentrated CO_2 from ammonia production process is estimated to be \$50/tCO_2 and it increases to around \$80/tCO_2 when capturing from the diluted flue gases (IEA, 2020a).

Table 6. Summary data for several low-carbon technologies for ammonia production

Mitigation lever route	Technology	TRL	Energy intensity (GJ/t-NH_3)	CO_2 emission intensity (t/t-NH_3)	CAPEX (2020 \$/t-NH_3)	Levelized cost (2020 \$/t-NH_3)
Feedstock switching	Water electrolysis for hydrogen	7-9	36 (IEA, 2021a)	0* (IEA, 2021a)	1160 (IEA, 2020b)	950 (IEA, 2021a)
Fuel & feedstock switching	Electrochemical synthesis	1-3	19.9 (Smith et al., 2020)	0* (Smith et al., 2020)	N/A	N/A
Feedstock switching	Biomass gasification for hydrogen	6-8	46.4(Gençer et al., 2020)	0.7-1.5 (Sánchez et al., 2019)	6320 (IEA, 2020b)	900 (IEA, 2021a)

*Renewable electricity used in the water electrolysis is assumed to be zero emissions.

Potential and Barriers

The low-carbon technologies of ammonia synthesis may overcome some of the issues associated with the traditional Haber–Bosch process, such as the large amount of CO_2 emissions and high fuel cost associated with steam reforming plant for hydrogen. However, the major challenge for these technologies is to overcome the need for large scales for the ammonia production and high production cost. The International Energy Agency Ammonia Technology Roadmap (IEA, 2021a) reports that the average levelized cost of ammonia production from the water electrolysis-based plant is around \$820/t-NH_3, which is roughly \$400/t-NH_3 higher than the cost of the conventional ammonia production. A technology report from DECHEMA implied that the production costs for ammonia, methanol, olefins and BTX (aromatics) using electrolysis would be two to five times higher than their fossil alternatives under current conditions (Bazzanella et al., 2017). Moreover, the electrochemical synthesis is hampered by the lack of a suitable cathode material that can selectively catalyze N_2 to NH_3 at practically usable production rates (Dražević & Skúlason, 2020). There are opportunities for capturing and utilizing the remaining 64% of pure CO_2 from the ammonia synthesis process as feedstocks to produce other primary chemicals and plastics. For instance, pure CO_2 can be used to produce methanol by thermal hydrogenation. Subsequently, methanol can be converted to the primary raw materials for plastic materials, such ethylene and propylene (Meys et al., 2021). Since CCU technologies rely on electricity as an important energy input, the barrier of increasing the use of CCU technology to produce primary chemicals and plastics mainly depends on the carbon intensity of electricity. Meys et al. (2021) concluded that the optimal electricity carbon footprint of 8.6 g CO_2 eq per kWh can help the global plastic industry deploy CCU, biomass utilization, and plastic recycling technologies to achieve the net-zero emissions. However, even in the most ambitious scenarios of IEA (IEA, 2021b), renewable electricity footprint is estimated to be 13.5 g CO_2 eq per kWh. Moreover, the additional investment cost of transport infrastructure for moving compressed CO_2 from the ammonia plant to the plastic manufacturing plant should be considered. There are other aspects of uncertainty in the decarbonization pathway of the ammonia industry, such as future costs of production and the pace of technology innovation. For example, ammonia production plants with CCS technology configuration could have lower deployment in some regions due to insufficient buildout of CO_2 transport and storage infrastructure (IEA, 2021a). Furthermore, it could be challenging to increase the deployment of electrolytic-based ammonia production since a significant amount of electricity would be required for this ammonia production process. For example, an additional 1200 TWh of electricity is needed for pursuing 100% electrolytic-based ammonia production to achieve net-zero emission compared to the original Net Zero Emission scenario with a 41% share of electrolytic-based ammonia production (IEA, 2021a). In order to overcome these technical and economic barriers, more mature technology innovations should be invented and implemented in an optimal way to reduce carbon emissions for the ammonia industry associated with a lower investment cost.

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