Life cycle energy use and greenhouse gas emissions of ammonia production from renewable resources and industrial by-products

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Life cycle energy use and greenhouse gas emissions of ammonia production from renewable resources and industrial by-products

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†Systems Assessment Center, Energy Systems Division, Argonne National Laboratory

Keywords: ammonia production, life cycle analysis, greenhouse gases, energy use

Abstract

Conventionally, ammonia is produced from natural gas via steam methane reforming (SMR), water-gas shift reaction, and the Haber-Bosch process. The process uses fossil natural gas, which leads to 2.6 metric tons of life cycle greenhouse gas (GHG) emissions per metric ton of ammonia produced. With ammonia being the second most produced chemical in the world, its production accounts for approximately 2% of worldwide fossil energy use and generates over 420 million tons of CO₂ annually. To reduce its carbon intensity, ammonia synthesis relying on renewable energy or utilizing by-products from industrial processes is of interest. We conduct a life cycle analysis of conventional and alternative ammonia production pathways by tracking energy use and emissions in all conversion stages, from the primary material and energy resources to the ammonia plant gates. Of all the alternative pathways, obtaining N₂ from cryogenic distillation and H₂ from low-temperature electrolysis using renewable electricity has the lowest cradle-to-plant-gate GHG emissions, representing a 91% decrease from the conventional SMR pathway.

1. Introduction

Ammonia is the second most produced chemical in the world nowadays.¹ Most of the ammonia produced was used for nitrogen fertilizer manufacture.² However, research suggests ammonia as a promising zero-carbon energy carrier because of its high volumetric energy density, which is approximately twice as high as that of liquid hydrogen (H₂). Moreover, ammonia stays in liquid form at...
room temperature and low pressure (~10 bar); while the liquefaction of H$_2$ requires cooling to -253°C and
approximately 12 kWh of electricity per kilogram (kg) of H$_2$ produced. The safe handling and
transportation infrastructure of ammonia are already in place, which may facilitate the transformation to
an expanded ammonia-based energy sector.

Ammonia is also being explored for long-term energy storage to enable greater penetration and
utilization of intermittent renewable wind and solar energy sources. Ammonia can play an essential role
in a future energy landscape with increased penetration of renewables by balancing the temporal
discrepancy between the supply of and demand for energy in various regions.

With these emerging applications of ammonia, future global production for ammonia could
increase by orders of magnitude. Conventionally, ammonia is produced from steam methane reforming
(SMR) of fossil natural gas or gasification of coal; these account for 72% and 22% of global ammonia
production capacity, respectively. Other feedstocks for ammonia production include fuel oil (4%) and
naphtha (1%). Ammonia production accounts for approximately 2% of worldwide fossil energy use and
generates over 420 million tons of CO$_2$ annually, representing 1.2% of the global anthropogenic CO$_2$
emissions. To decarbonize the ammonia sector, alternative ammonia production pathways from
renewable sources are of increasing interest.

With current technologies, it is feasible to produce ammonia from carbon-free resources — water
and air — using renewable electricity as the main energy source for air separation and water
electrolysis. For example, a commercial plant recently built by Yara, a nitrogen fertilizer manufacturer,
demonstrated the use of renewable electricity to split water into H$_2$ and O$_2$ and the Haber-Bosch (HB)
reaction to combine H$_2$ and N$_2$ to produce low-carbon ammonia. Morgan et al. conducted two techno-
economic analyses of wind-powered ammonia production to demonstrate the process’s economic
feasibility.

One of the most-used techniques for environmental assessment of any product is life cycle
analysis (LCA). LCA holistically evaluates the environmental impacts of a product by compiling an
inventory of energy and material inputs to the various stages along the product’s life cycle and calculating the associated resource use and resulting emissions.  

LCA has been widely applied to evaluate conventional ammonia production pathways.  
Johnson et al. assessed the life cycle energy use and greenhouse gases (GHG) emissions from SMR of fossil natural gas in the U.S., using industry-aggregated inventory data. Zhang et al. quantified the life cycle GHG emissions resulting from China’s nitrogen fertilizer production and consumption supply chain, with a focus on using prevailing technologies to produce ammonia, such as natural gas SMR and coal gasification. Bicer et al. assessed the use of fossil resources, such as coal, natural gas, and heavy oil, to produce ammonia and reported the global warming potential (GWP) for a period of 500 years. They concluded that using electricity generated from fossil resources for H₂ production via water electrolysis would incur more life cycle GHG emissions than the natural gas SMR pathway.

Only few studies applied LCA to assess alternative low-carbon ammonia production pathways, although alternative low-carbon ammonia production technologies utilizing renewable electricity have been extensively studied. Bicer et al. compared the life cycle energy and exergy efficiency, as well as the GHG emissions, of various ammonia production pathways employing the HB reaction and H₂ from water electrolysis and using zero- or low-carbon electricity from municipal waste, nuclear, biomass, and hydropower. In another LCA study, Bicer and Dincer evaluated the impacts of different end-use applications of ammonia produced from an electrochemical pathway, such as city transportation and power generation. In these two LCA studies, H₂ was assumed to be produced from water electrolysis and N₂ from cryogenic distillation. However, other large-scale potential sources of H₂ have not been assessed, for example, H₂ as industrial by-products. Moreover, other air separation techniques have not been analyzed.

In this paper, we extend the work of Bicer et al. and Zhang et al. by using LCA to assess additional low-carbon technology pathways to produce syngas containing the N₂ and H₂ needed by the
HB loop for ammonia synthesis. We evaluate two technologies for producing N\textsubscript{2}: cryogenic distillation (CD) and pressure swing adsorption (PSA), and four technology pathways to produce H\textsubscript{2}: low-temperature electrolysis (LTE), high-temperature electrolysis (HTE), as a by-product from chlor-alkali (CA) processes, and as a by-product in steam cracker (SC) plants. In addition, this work provides a detailed energy and emission inventory for each stage in the ammonia life cycle for each of the technology pathways considered. This work also assesses the sensitivity of energy use and GHG emissions to the source of electricity, key process parameters, and co-product treatment methods.

2. Ammonia manufacturing technology description and evaluation of system boundary

Our LCA system boundary is cradle-to-plant-gate, and the functional unit is 1 metric ton of ammonia produced. We utilized the Greenhouse gases, Regulated Emissions, and Energy use in Technologies (GREET\textsuperscript{®}) model (2019) to conduct the LCA.\textsuperscript{20,21} We evaluate energy use and GHG emissions associated with ammonia production pathways, here referred to as the “cradle-to-plant-gate life cycle.” Those related to equipment manufacturing, e.g., reactors or electrolytic cells, are likely to be small considering the ammonia throughput over the life of a production plant, and are thus kept out of scope for this analysis. The goal is to evaluate the life cycle GHG emissions of ammonia produced from alternative low-carbon pathways in comparison with the conventional natural gas SMR pathway.

We assume that the H\textsubscript{2} plant, N\textsubscript{2} plant, and HB plant are co-located. Moreover, since our study of the ammonia production pathways ends at the ammonia plant gate, the storage, transportation, and end use of ammonia are not included in the scope of analysis. The cradle-to-plant-gate GHG emissions are presented in CO\textsubscript{2} equivalents (CO\textsubscript{2e}) of CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2}O with their 100-year GWP of 1, 30, and 265, respectively, following the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report.\textsuperscript{22}
Conventional ammonia production based on steam methane reforming

Conventionally, ammonia is produced from SMR of natural gas. There are two main functional steps in this pathway: The first is to produce H₂ from natural gas via steam methane reforming, and the second is to synthesize ammonia via the HB process, as depicted in Figure 1. In the natural gas supply in North America, which is the focus of this study, the shares of conventional and shale gas are 48% and 52%, respectively.

Figure 1: Process diagram for conventional ammonia production (adapted from Johnson et al.

Methane (CH₄) is reformed with steam at up to 1000°C in the primary and secondary SMR reactors to form H₂ and carbon monoxide (CO) according to Reaction 1:

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \]  

Compressed air is introduced into the secondary SMR reactor to combust a portion of the natural gas to provide heat of reaction. Oxygen (O₂) is depleted during the combustion, while the stoichiometric nitrogen (N₂) is used in the downstream HB synthesis loop, avoiding the need for an air separation unit (ASU) in this pathway. The gas mixture at the SMR reactor outlet contains H₂, CO, CO₂, unreacted steam, and CH₄, and is cooled and sent to a two-stage water-gas shift (WGS) reactor to increase the H₂ yield, according to Reaction 2:

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]  

Mono-ethanol-amine scrubbing or the Selexol process is employed to remove CO₂, and methanation converts the remaining CO into CH₄ to prevent poisoning of the HB catalyst. After
compression, the syngas mixture enters the HB loop, where stoichiometric N\textsubscript{2} and H\textsubscript{2} react at 150–250 bar and 400°C–450°C with the presence of iron-based catalyst to produce ammonia according to Reaction 3:

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]  

Recycling is needed, since the single-pass conversion rate for ammonia is low (around 15%). Ammonia is condensed and separated at -25°C to -33°C. The unreacted N\textsubscript{2} and H\textsubscript{2} are compressed and recycled to the HB reactor. Heat recovered from the cooling of the gas mixture exiting the secondary SMR reactor is used to raise the temperature of the steam, which is expanded in the steam turbine to drive the compression of air fed into the secondary SMR reactor and feed gas introduced to the HB synthesis loop. Therefore, the modern ammonia manufacturing process is highly integrated.

The inventory of this integrated pathway was incorporated into the GREET model, as summarized in Table 1, and used for this analysis without modification.\textsuperscript{20} The cradle-to-plant-gate GHG emissions for this pathway are 2.6 metric ton CO\textsubscript{2e}/metric ton ammonia,\textsuperscript{20,23} which agrees well with the range reported in Zhang et al. (2.1–3.6 metric tons CO\textsubscript{2e} per metric ton NH\textsubscript{3}).\textsuperscript{11} For comparison, the cradle-to-plant-gate GHG emission of the coal gasification pathway to produce ammonia is 6.1–7.8 metric tons CO\textsubscript{2e} per metric ton NH\textsubscript{3}, which is much higher than the natural gas SMR pathway.\textsuperscript{11} Our results are less comparable with those in Bicer et al.,\textsuperscript{12} since they reported the GWP for a period of 500 years while we calculated the 100-year GWP.

**Alternative ammonia production**

In addition to the natural gas SMR pathway, there are alternative technologies for ammonia manufacturing. The basic structure of these alternative pathways is depicted in Figure 2. High purity N\textsubscript{2} is obtained by separating air, and high purity H\textsubscript{2} can be produced from various technologies, as explained below.
Figure 2: Process diagram for alternative ammonia production pathways.

The gas mixture containing stoichiometric N\textsubscript{2} and H\textsubscript{2} is compressed to the operating pressure of the HB reactor (assumed to be 200 bar in this analysis) and enters the electricity-driven HB synthesis loop. As with the conventional pathway, the single-pass conversion rate for ammonia is only 15%, so recycling of unreacted syngas is needed. There is a pressure drop around the HB synthesis loop, which is assumed to be 6% of the operating pressure of HB reactor.\textsuperscript{3,24} Thus, for a HB reactor pressure of 200 bar, the single-pass pressure drop is approximately 12 bar. To overcome this pressure drop, the recycled gas mixture needs to be recompressed to the operating pressure of the HB reactor. In the HB synthesis loop, the electricity is required almost exclusively for syngas/recycle gas compression.\textsuperscript{3,7} The synthesis loop does not need an external heat source, since the HB reaction is exothermic, and the utilization of reaction heat through heat integration is sufficient to satisfy the process heat demand.\textsuperscript{14,25} Pumping energy is also required to circulate cooling water. According to Morgan et al.,\textsuperscript{7} the pumping power only accounts for ~1% of the total power required in the synthesis loop, so it is considered negligible and not included in this analysis.

It is worth mentioning that the HB loop, including the syngas compression, needs to be supplied with constant power. Therefore, in this analysis, we assume that the HB loop utilizes grid electricity to power the electric motors that drive gas compressors. For a large pressure increase, a multi-stage compressor should be used with an intercooler between stages to reduce the compression power and keep the compression discharge temperature below a practical limit. Equation 4 is applied to calculate the compression energy:
\[ E_{\text{comp}} = \frac{1}{3600} \times \frac{1}{\eta_{\text{EM}}} \times n \times Z \times R \times T \times \frac{1}{\eta_{\text{c}}} \times \frac{k}{k - 1} \times \left[ \left( \frac{P_{\text{outlet}}}{P_{\text{inlet}}} \right)^{\frac{k-1}{k}} - 1 \right] \]  

Equation 4

where \( E_{\text{comp}} \) is the energy required for gas compression in the unit of kWh/kg gas, \( \eta_{\text{EM}} \) is the electric motor efficiency, assumed to be 95% in this analysis, and \( n \) is the number of compression stages, determined by the outlet pressure (\( P_{\text{outlet}} \), in units of bar or psi), the inlet pressure (\( P_{\text{inlet}} \), in the unit of bar or psi), and the compression pressure ratio per stage. In this analysis, we assume the per-stage compression ratio is 2 for both \( \text{N}_2 \) and \( \text{H}_2 \). \( Z \) is the compressibility factor, assumed to be 1 in this analysis, \( R \) is the gas constant (0.297 kJ/kg-K for \( \text{N}_2 \), 4.125 kJ/kg-K for \( \text{H}_2 \), and 0.978 kJ/kg-K for syngas), \( T \) is the inlet gas temperature in degrees Kelvin, \( \eta_{\text{c}} \) is the isentropic efficiency of compression, assumed to be 80% in this analysis, and \( k \) is the specific heat ratio (1.4 for \( \text{N}_2 \) and \( \text{H}_2 \)).

Applying Equation 4, the electric energy required by the HB loop is 0.324 kWh/kg \( \text{NH}_3 \). This value is comparable to those reported in literature. Frattini et al. reported a compression power demand of 0.44 kWh/kg \( \text{NH}_3 \) using an Aspen Plus simulation,\(^{14}\) while Morgan et al. reported the energy required by the HB synthesis loop to be approximately 0.64 kWh/kg \( \text{NH}_3 \) based on literature values.\(^{7,24}\) These differences may stem from the variations in process specifications: pressures at which syngas \( \text{N}_2 \) and \( \text{H}_2 \) are produced, assumed compression efficiency, assumed electric motor efficiency, pressure of the HB reactor, and pressure drop in the HB loop.

Various technologies for \( \text{N}_2 \) production from air separation

There are three main methods of separating \( \text{N}_2 \) from air: cryogenic distillation, pressure swing adsorption (PSA), and membrane separation. Membrane separation cannot achieve a purity level high enough for ammonia production, especially at a high flowrate\(^{14}\) and without a deoxygenator.\(^{7}\) Moreover, \( \text{O}_2 \) cannot be recovered as a co-product with membrane separation.\(^{26}\) Therefore, we focus on the other two technologies in this analysis.
Cryogenic distillation

Cryogenic distillation accounts for more than 90% of the global production of N\textsubscript{2}.\textsuperscript{26} It is suitable for large system production with impurity concentrations down to the parts-per-billion range.\textsuperscript{26} Compared to other air separation methods, cryogenic distillation produces the purest N\textsubscript{2} and requires the smallest input power.\textsuperscript{26} Cryogenic distillation works by utilizing the differences in boiling point of major air components: Air is cooled down to its dew point while the contaminants are removed, and then distilled into its individual components with a distillation column. The energy requirement for separating one standard cubic meter of pure N\textsubscript{2} at 8 bar ranges from 0.15 to 0.25 kWh, which is bound by two modifications to the double-column system. In this analysis, we use a mid-value of 0.2 kWh/m\textsuperscript{3} at standard temperature (0 °C) and pressure (1 bar) (STP). With the density of N\textsubscript{2} at STP equal to 1.23 kg/m\textsuperscript{3}, 162 kWh of electricity is consumed per metric ton N\textsubscript{2} produced.\textsuperscript{26} Since the liquefaction of air occurs at low temperatures and requires a steady energy supply, we assume for the base design case that the cryogenic distillation of air to produce N\textsubscript{2} utilizes grid electricity.

Pressure swing adsorption

PSA is suitable for small system production, with N\textsubscript{2} purity up to 99.99%.\textsuperscript{26} A N\textsubscript{2}-PSA plant utilizes carbon molecular sieves, which in the adsorption mode preferably adsorb H\textsubscript{2}O, CO\textsubscript{2} and O\textsubscript{2} while letting N\textsubscript{2} pass through into a buffer tank. In the adsorbent regeneration mode, the pressurized gas in the adsorber is released to the atmosphere. The N\textsubscript{2} collected in the buffer tank serves as the final product. The PSA unit is more flexible in the context of renewable energy utilization, since it only needs a few minutes to reach its full production capacity. This feature is particularly useful when the energy supply for producing N\textsubscript{2} fluctuates significantly, as is the case with intermittent renewable energy. In contrast, the cryogenic ASU needs two hours before it starts to steadily produce N\textsubscript{2} and O\textsubscript{2}. It is estimated that 365 kWh of electricity is required to produce a metric ton of nitrogen at 8 bar, which is a typical operating pressure for N\textsubscript{2}-PSA unit.\textsuperscript{26}
Various technologies for H₂ production

Four alternative H₂ production technologies are evaluated in this study, all of which satisfy the H₂ purity requirement for the HB process and supply H₂ at 20 bar.²⁰

By-product H₂ from chlor-alkali processes

H₂ may be available as a by-product from the chlor-alkali (CA) process, which coproduces sodium hydroxide and chlorine as main products via electrolysis of a sodium chloride solution. Reactions 5 and 6 occur at cathode, while 7 and 8 occur at anode. Reaction 9 represents the overall reaction.²⁷

\[
\begin{align*}
2H_2O + 2e^- &\rightarrow H_2 + 2OH^- \\
2Na^+ + 2OH^- &\rightarrow 2NaOH \\
2NaCl &\rightarrow 2Na^+ + 2Cl^- \\
2Cl^- &\rightarrow Cl_2 + 2e^- \\
2NaCl + 2H_2O &\rightarrow Cl_2 + 2NaOH + H_2
\end{align*}
\]

Hydrogen as a by-product from CA plants is vented if not sold for industrial use.¹⁹,²⁰ The CA process is a mature industrial technology capable of co-producing high-purity H₂ on a large scale (up to ~ 0.4 million tons per year) and at a relatively low price (~ $1/kg H₂).¹⁹ H₂ produced from the CA process is of high purity (>99.9%), obviating the need for an additional purification process. Therefore, the post-processing of H₂ only requires cooling/drying and compression. From a H₂ production standpoint, electricity is needed for electrolysis of the sodium chloride solution and compression of H₂, while heat is required to process the sodium chloride solution. Electricity can be sourced from the grid or an onsite combined heat and power (CHP) system. If the CA process has a CHP system, then the process heat demand can be met solely by the recovered heat from the CHP. Otherwise, the process heat is provided by natural gas boilers. A detailed process inventory is available in Lee et al., where four H₂ co-product treatment methods are assessed: venting, combustion/substitution, mass allocation, and market value allocation.¹⁹,²⁷ In this study, we assume that there is no on-site CHP and consider three treatments of by-
product H$_2$ — venting (as the base design case), combustion/substitution and mass allocation (as sensitivity cases) — which cover the two extremes in terms of cradle-to-plant-gate GHG emissions. If the CA plant is designed to vent by-product H$_2$, it is treated as waste. However, if the CA plant is designed to use byproduct H$_2$ for process heat, then the thermal energy in the H$_2$ exported for ammonia production must be replaced by an equivalent thermal energy, which we assume to be sourced from natural gas.

*By-product H$_2$ from steam cracking of natural gas liquids (NGLs)*

By-product H$_2$ from the steam cracking (SC) of NGLs has been of interest recently due to increased shale gas production. It is estimated that 3.5 million tons of by-product H$_2$ can be available annually from steam cracker plants. Steam cracker plants use thermal cracking of hydrocarbon feedstock, such as NGLs, to produce light olefins and other co-products. As shown in Reaction 10, H$_2$ is available as a by-product of the cracking process.

\[
C_nH_{2n+2} + \text{steam} \xrightarrow{\text{heat}} aH_2 + bCH_4 + cC_2H_4 + dC_3H_6 + eC_4H_8 + fC_5 + \]

The heat required for cracking is usually provided by combusting a mixture of by-product H$_2$, natural gas, and/or surplus CH$_4$ from the cracking process. Alternatively, by-product H$_2$ may be separated for export to other markets (e.g., ammonia production), and its heating value can be replaced with combusting additional natural gas. The cracked gas is usually post-processed through quenching, compression, and fractionation to separate the mixture into individual products. PSA can be employed to separate and purify by-product H$_2$ to meet the requirements of the HB process. The energy intensity of the PSA unit is estimated at 0.5 kWh/kg H$_2$. A detailed process inventory is available in Lee et al. Two co-product treatment methods are considered: substitution (as the base case) and mass allocation (as a sensitivity case). The substitution method is similar to what has been described above for the CA process, since most steam cracker plants combust by-product H$_2$ on site for process heat. For mass allocation, the mass balance between products is used to allocate environmental burdens.
Low-temperature electrolysis (LTE) from renewable electricity

There are two common water electrolyzer technologies used in low-temperature applications: alkaline and proton exchange membrane (PEM). Both are mature technologies and have the potential to produce H\(_2\) at a large scale, but the latter is more suitable for use with intermittent renewables due to its fast response rate.\(^5,16\)

As its name suggests, alkaline electrolysis employs a 25%–30% aqueous KOH solution as the electrolyte in which the electrodes are immersed, separated by a diaphragm.\(^28\) Reactions 11 and 12 represent the reactions occurring at the cathode and anode, respectively, with a direct current application:

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (11)
\]

\[
2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \quad (12)
\]

H\(_2\) is produced at the cathode with a high purity, typically ranging from 99.5%–99.9% after drying. The system energy efficiency of the alkaline electrolyzer is in the range of 51%–60% based on the lower heating value of H\(_2\).

PEM electrolysis utilizes a solid proton-conducting membrane stack on which the electrodes are usually directly mounted. Reactions 13 and 14 represent the reactions taking place at the cathode and anode, respectively. Both reactions happen in the acidic regime, in contrast to those of alkaline electrolysis.

\[
2H^+ + 2e^- \rightarrow H_2 \quad (13)
\]

\[
H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \quad (14)
\]

PEM electrolysis produces H\(_2\) at the cathode with a purity over 99.99%, due to the very low permeation across the PEM. A PEM electrolyzer cell can operate under higher current density (>1500 milliamps per square centimeter [mA/cm\(^2\)]) than the alkaline electrolyzer cell (200-600 mA/cm\(^2\)), which supports the higher-pressure operation of PEM electrolysis and reduces the downstream burden to compress the syngas at the HB reactor.\(^{16,28}\)
PEM electrolyzer technology has an energy efficiency of up to 72%.\textsuperscript{20} In this analysis, we assume that PEM electrolyzer energy efficiency is 63% based on a lower heating value of H\textsubscript{2}, meaning that 63% of the input electric energy would be stored in the H\textsubscript{2} product in the form of chemical energy (lower heating value).\textsuperscript{20} The electricity for electrolysis is assumed to be sourced from renewable resources, such as wind or solar. However, to balance the supply and demand of intermittent and geographically isolated renewable electricity, storage equipment, such as an H\textsubscript{2} storage tank and/or battery, is needed to enable a consistent H\textsubscript{2} supply to the HB loop. This may increase the capital investment and impact the cost of the ammonia produced, which is beyond the scope of this analysis.

*High-temperature electrolysis with solid oxide electrolysis cell*

A solid oxide electrolysis cell (SOEC) is used for high-temperature electrolysis (HTE) applications due to its ability to withstand high temperatures. H\textsubscript{2} production from high-temperature electrolysis using SOEC provides higher electrical energy efficiency than low-temperature electrolysis, since part of the total process energy requirement is satisfied by heat rather than electricity.\textsuperscript{6} In this analysis, we assume that the required heat and electricity are provided by a high-temperature gas-cooled reactor (HTGR) using uranium (U-235) as fuel. The upstream energy use and emissions associated with uranium mining, conversion, enrichment, and transportation are estimated by the GREET model.\textsuperscript{20,30} In the HTGR, heat is generated to increase the temperature of steam entering the SOEC to approximately 800°C. The remaining heat drives a high-efficiency gas turbine to produce electricity for the electrolysis process. Reactions 15 and 16 represent the reactions at the cathode and anode of SOEC, respectively.\textsuperscript{28}

\begin{equation}
H_2O + 2e^{-} \rightarrow H_2 + O^2- \quad (15)
\end{equation}

\begin{equation}
O^2- \rightarrow \frac{1}{2}O_2 + 2e^{-} \quad (16)
\end{equation}

H\textsubscript{2} is produced at the cathode and separated from the steam by cooling and condensation of water.

For both water electrolysis pathways, LTE and HTE, the overall reaction is the same and is given by Reaction 17:

\begin{equation}
H_2O \rightarrow \frac{1}{2}O_2 + H_2 + 2e^- \quad (17)
\end{equation}
According to the reaction stoichiometry, when producing 1 kg of $H_2$, 7.9 kg of $O_2$ is produced as a by-product. In this analysis, no credits have been given to by-product $O_2$ from $N_2$ production from air or $H_2$ production from water.

Table 1: Inventories for conventional and alternative ammonia production

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* 28.3% of the total natural gas input is used as fuel.
** A thermal-to-hydrogen efficiency of 50% is used.31

3. Results and Discussion

Cradle-to-plant-gate fossil energy consumption

Figure 3 shows the cradle-to-plant-gate fossil energy consumption for various ammonia production pathways. The conventional SMR pathway consumes the highest amount of fossil energy because it uses mainly fossil natural gas as feedstock and process fuel.
Figure 3: Cradle-to-plant-gate fossil energy consumption in base case co-product treatment methods. Electricity source for N\textsubscript{2} production and HB loop: 2019 U.S. grid generation mix. “Energy use in HB loop” represents the fossil energy consumed for producing and using natural gas and/or electricity in the HB loop.

For the alternative ammonia production pathways, preparing syngas via N\textsubscript{2}-CD and H\textsubscript{2}-LTE consumes the least fossil energy per metric ton of NH\textsubscript{3} produced, a 93% reduction from the conventional SMR pathway. This is because most of the energy in this pathway is required for H\textsubscript{2} production, and we assume that renewable electricity generated from solar or wind is used for this process. The majority of the energy consumed when producing H\textsubscript{2} via HTE is also non-fossil, since this process utilizes nuclear energy for both heat and power. For H\textsubscript{2} produced from the CA process, more fossil energy is consumed than in water electrolysis, which sources renewable electricity, since the U.S. grid mix is assumed to be used in the CA process for the cooling/drying and compression of H\textsubscript{2}. Of the 2019 U.S. grid mix, 63% is generated from fossil resources — coal and natural gas. A significantly higher amount of fossil energy is consumed in the H\textsubscript{2}-SC pathways as a result of the substitution method used to evaluate by-product H\textsubscript{2} in the base case, as mentioned earlier. In that method, natural gas combustion is assumed to substitute for the heat loss resulting from selling byproduct H\textsubscript{2}. However, even in this scenario, the ammonia production consumes 32% less fossil energy than the conventional SMR pathway.
Cradle-to-plant-gate GHG emissions

Figure 4 depicts the cradle-to-plant-gate GHG emissions for various ammonia production pathways.

Figure 4: Cradle-to-plant-gate GHG emissions in base case co-product treatment methods. Electricity source for N₂ production and HB loop: 2019 U.S. grid generation mix. The “conversion-related process emission” from the conventional SMR pathway consists of CO₂ generated from WGS reactor per Reaction 2. “Energy use in HB loop” represents the emissions associated with producing and using energy in the HB process, which includes GHG emissions from natural gas combusted in industrial boilers to provide process heat.

Figure 4 shows that all alternative pathways generate lower cradle-to-plant-gate GHG emissions than the conventional SMR pathway. Of all the alternative pathways, obtaining N₂ from cryogenic distillation and H₂ from LTE using renewable electricity has the lowest cradle-to-plant-gate GHG emissions, representing a 91% decrease from the conventional SMR pathway.

The contribution of N₂ production to cradle-to-plant-gate GHG emissions varies among different ammonia production pathways. For the pathway where N₂ production has the highest contribution to the cradle-to-plant-gate GHG emissions (N₂-PSA and H₂-LTE), it accounts for 48% of the total emissions. This is because producing N₂ via PSA is more energy intensive than cryogenic distillation (Table 1) and H₂ produced from renewable electricity powered LTE does not contribute to GHG emissions. It is noteworthy that for the conventional SMR pathway, N₂ in the syngas is not produced with ASU but by
depleting the O$_2$ in the air during natural gas combustion for process heat, and thus does not explicitly contribute to cradle-to-plant-gate GHG emissions.

In this analysis, we assume that all the alternative pathways use a common HB process to produce NH$_3$, which consumes 1.165 GJ of U.S. grid electricity per metric ton NH$_3$ and leads to 0.156 metric tons GHG/metric ton NH$_3$. For pathways where H$_2$ is produced mainly from non-fossil sources (LTE and HTE), this emission translates into a 48% to 71% contribution to the cradle-to-plant-gate GHG emissions. However, if H$_2$ is a by-product from the steam cracker plant under the substitution co-product treatment method, this emission contributes only 9% to the overall life cycle emissions.

**Sensitivity analysis**

**Regional electricity generation mix**

Figure 5 shows the impact of the regional utility grid generation mix on the cradle-to-plant-gate GHG emissions for ammonia production. Here, we assume that N$_2$ is produced via cryogenic distillation and ammonia is produced via HB using the regional grid generation mix. For electricity consumed in various H$_2$ production pathways (e.g., H$_2$-CA and H$_2$-SC), we also assume that regional grid generation mix is used.

There are eight major electricity regions in the contiguous U.S., which have different shares of electricity generation technologies. The GHG emission intensity of different regional grid generation mixes is shown in Figure 5. A lower GHG emission intensity for the electricity generation mix results in lower cradle-to-plant-gate GHG emissions for ammonia.

Figure 5 demonstrates that if the Northeast Power Coordinating Council (NPCC) grid mix is used to prepare syngas via N$_2$-CD and H$_2$-LTE, instead of the U.S. average grid mix, the cradle-to-plant-gate GHG emission per metric ton of ammonia produced can be reduced by 44%. This is because the NPCC grid has the largest share of near-zero-carbon nuclear and hydro power generation of all utility regions. 

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Figure 5: Impact of regional electricity grid generation mix and co-product treatment method on cradle-to-plant-gate GHG emissions of various ammonia production pathways. The grey horizontal line represents the cradle-to-plant-gate GHG emissions of the conventional SMR pathway in the context of 2019 U.S. grid generation mix. Regional electric grids: Western Electricity Coordinating Council (WECC), Midwest Reliability Organization (MRO), Southwest Power Pool (SPP), Texas Reliability Entity (TRE), SERC Reliability Corporation (SERC), Florida Reliability Coordinating Council (FRCC), Reliability First Corporation (RFC), and Northeast Power Coordinating Council (NPCC).

Figure 5 also shows that if grid electricity is used to produce H$_2$ via LTE (H$_2$-grid mix-LTE), the cradle-to-plant-gate GHG emissions would increase by a factor of 21 over using renewable electricity from solar/wind to power H$_2$-LTE, exceeding those from the conventional SMR pathway. This finding suggests using electricity generated mainly from fossil resources to electrolyze water to produce H$_2$ needed for the HB process would increase life cycle GHG emissions compared to the natural gas SMR pathway, which agrees well with previous findings in the literature.$^{12}$

Therefore, the carbon intensity of the electricity used to power all processes in the ammonia production pathway is crucial for the cradle-to-plant-gate GHG emissions associated with ammonia production. In this analysis, we assume that grid electricity is used to power N$_2$-CD and ammonia-HB, since these processes require a steady energy supply to operate in the continuous mode. The cradle-to-
plant-gate GHG emissions of ammonia can be further reduced if renewable electricity can be supplied continuously to provide the energy required by N\textsubscript{2} production and the HB synthesis loop. In that case, the ammonia produced can be carbon-free. However, mitigating the intermittency of renewable resources such as wind and solar would require energy storage, which impacts the economics of their supply and thus the economics of ammonia production.

Co-product treatment methods for H\textsubscript{2} production

Figure 5 also illustrates the impact of the H\textsubscript{2} by-product treatment method on the cradle-to-plant-gate GHG emissions for various ammonia production pathways.

For byproduct H\textsubscript{2} from CA plants, using the substitution co-product treatment method results in higher cradle-to-plant-gate GHG emissions (1.84 metric tons GHG/metric ton ammonia) than the venting treatment (0.37 metric ton GHG/metric ton ammonia), due to the additional natural gas used to substitute for the energy in the exported H\textsubscript{2}. Employing mass allocation instead of venting slightly increases the cradle-to-plant-gate GHG emissions (0.51 metric ton GHG/metric ton ammonia). This is because instead of being treated as a waste, as in mass allocation, the environmental burdens of the CA plant are distributed between sodium hydroxide, chlorine, and H\textsubscript{2} based on their mass shares in the total plant mass output.

A similar conclusion can be drawn for byproduct H\textsubscript{2} from steam cracker plants: The substitution co-product treatment method leads to higher cradle-to-plant-gate GHG emissions than the mass allocation treatment. Despite the co-product treatment methods, the life cycle GHG reduction benefits of all alternative ammonia production pathways using by-product H\textsubscript{2} are robust compared to the conventional SMR pathway.

Key process parameters

In this analysis, the assumptions for key process parameters are shown in Table 2. We assess how varying these parameters within predefined ranges affects the cradle-to-plant-gate GHG emissions of
ammonia. Electrolyzer efficiency for H₂-LTE has not been included, since renewable electricity from solar/wind is assumed to power water electrolysis, and thus the efficiency value is inconsequential to GHG emissions.

Table 2: Key process parameters and their potential ranges assumed for stochastic analysis

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB reaction pressure</td>
<td>200</td>
<td>150 – 250</td>
</tr>
<tr>
<td>Pressure drop in the HB loop</td>
<td>6%</td>
<td>3% – 10%</td>
</tr>
<tr>
<td>Single-pass conversion rate in HB loop</td>
<td>15%</td>
<td>10% – 35%</td>
</tr>
<tr>
<td>Electricity use for cryogenic ASU</td>
<td>0.2</td>
<td>0.15 – 0.25</td>
</tr>
<tr>
<td>Ammonia condensation temperature</td>
<td>-30</td>
<td>-25 – -33</td>
</tr>
</tbody>
</table>

We randomly sampled each parameter within its corresponding range 2000 times, assuming uniform distribution, and used the sampled values to generate the cradle-to-plant-gate GHG emission results. Figure 6(a) indicates that the assumed ranges of key process parameters lead to a wide range in cradle-to-plant-gate GHG emissions from the N₂-CD and H₂-LTE pathway. The baseline value is 0.221 metric ton GHG/metric ton NH₃, as indicated by the dashed line, with a standard deviation of 0.015 metric ton GHG/metric ton NH₃. By decreasing the HB reactor pressure, reducing the pressure drop in the HB loop, increasing the single-pass conversion rate, and reducing the electricity consumption per unit of N₂ produced, the cradle-to-plant-gate GHG emission of ammonia can be reduced by 20% to 0.178 metric ton GHG/metric ton NH₃.

This is further confirmed by the sensitivity analysis shown in Figure 6(b), which shows the effect of varying each parameter within the specified range, one at a time. In the tornado plot, the x-axis indicates the percentage differences induced by each process parameter as compared to the baseline scenario. For the N₂-CD and H₂-LTE pathway to produce ammonia, the electricity consumed to produce one unit of N₂ is the most influential parameter. This is partly because in this pathway, the life cycle GHG emissions resulting from N₂ production contribute 29% to the life cycle results. Reducing the electricity
consumption from 0.2 to 0.15 kWh/m$^3$ N$_2$ produced can lower the cradle-to-plant-gate GHG emissions by 7.3%. Reducing the HB reaction pressure from 200 bar to 150 bar while maintaining the single-pass conversion rate leads to a 6.6% decrease in the cradle-to-plant-gate GHG emissions. Improving the single-pass conversion rate in the HB loop from 15% to 35% would reduce the cradle-to-plant-gate GHG emissions of ammonia production by 4.5%, since a higher single-pass conversion rate would reduce the amount of recycled syngas that needs to be recompressed. A single-pass conversion rate of 35%, instead of 15%, would reduce the size of the recycled syngas stream by two-thirds. Therefore, less energy would be required for recycled syngas recompression, if the single-pass pressure drop in the HB loop remains the same. With a lower single-pass pressure drop, the energy consumption for recycled syngas recompression would be further reduced.

![Figure 6: Impacts of assumptions on key process parameters on the cradle-to-plant-gate GHG emission of ammonia produced via N$_2$-CD and H$_2$-LTE.](Image)

4. Conclusion

In this study, we evaluated various ammonia production pathways in terms of their cradle-to-plant-gate energy use and GHG emissions. Four methods for syngas H$_2$ production were assessed. LTE using renewable electricity outperforms all other technology pathways for H$_2$ production with respect to cradle-to-plant-gate GHG emissions of ammonia. However, the successful deployment of this technology may require energy storage to buffer the intermittent renewable electricity, which may negatively impact
the economics of low-carbon ammonia production. Sourcing H₂ from HTE with SOEC using nuclear power can produce ammonia with low cradle-to-plant gate GHG emissions similar to sourcing H₂ from LTE using wind/solar electricity, but has the advantage of a steady supply of electricity (i.e., nuclear electricity), which may improve the economics of producing low-carbon ammonia. Utilizing the by-product H₂ from chlorine-alkali and steam cracker plants has the potential to produce ammonia at a large scale. However, the cradle-to-plant gate GHG emission of the ammonia produced depends on the co-product treatment method of by-product H₂. Two methods for syngas N₂ production are assessed: The PSA technology is more energy intensive but has a faster response rate than cryogenic distillation. The life cycle GHG reduction benefits of all alternative ammonia production pathways are robust compared to the conventional SMR pathway.

5. Conflicts of interest

There are no conflicts of interest to declare.

6. Acknowledgment

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