Towards Sustainable Ammonia Synthesis: A Critical Review of Alternative Methods to the Haber-Bosch Process

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Abstract

Ammonia is indispensable for global agriculture, industry and its emerging role as an energy carrier. However, its production remains dominated by the century-old Haber-Bosch process which consumes 1-2% of the world's total energy and contributes to 1.5-2% of global CO_2 emissions. This review analyses the current industrial standard and its limitations, and assesses the technical feasibility and potential of alternative pathways. These include electrocatalytic nitrate reduction, direct electrochemical nitrogen reduction, a renewable-powered Haber-Bosch process, photocatalytic nitrogen reduction and biological nitrogen fixation. Such approaches operate under milder conditions, utilizing renewable energy to reduce the reliance on fossil fuels. Although no single technology can yet fully replace the conventional Haber-Bosch process, advancements in catalyst designs, process engineering and renewable energy integration could enable large-scale green ammonia production in the future. Such developments would enhance global food security, reduce the environmental impact of carbon emission and energy consumption, and would contribute significantly to achieving climate targets.

Key words: Haber-Bosch process, Green ammonia technologies, Sustainable ammonia production, Carbon emission mitigation, Energy-efficient nitrogen fixation, Electrocatalytic nitrate reduction, Electrochemical nitrogen reduction, Renewable-powered Haber-Bosch process, Photocatalytic nitrogen reduction, Biological nitrogen fixation.

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All AI-assisted outputs were reviewed, edited, and verified by me to ensure factual accuracy and consistency with my intended meaning.

Finally, I declare that no AI-generated content has been presented as my own original work.

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Abbreviations

AEM	Anion Exchange Membrane
Ag@NiO/CC	Ag Nanoarray on NiO Nanosheets on Carbon Cloth
ASU	Air Separation Unit
CB	Conduction Band
CC	Carbon Cloth
Cu/CoP/NF	Copper/Cobalt Phosphide/Nickel Foam
ENR	Electrochemical Nitrate Reduction
FC	Fluorine-doped Carbon
FE	Faradaic Efficiency
H*	Atomic Hydrogen
h+	Positively Charged Hole
HER	Hydrogen Evolution Reaction
LPG	Liquid Petroleum Gas
MvK	Mars-van Krevelen
*N	Atomic Nitrogen
NF	Nickel Foam
NRR	Nitrogen Reduction Reaction
PEM	Polymer Electrolyte Membrane
PSA	Pressure Swing Adsorption
PTFE	Polytetrafluoroethylene
PV	Photovoltaic
RHE	Reversible Hydrogen Electrode

RPHB	Renewable-powered Haber-Bosch
SAC	Single Atom Catalyst
SMR	Steam Methane Reforming
VB	Valence Band

CHAPTER 1 – INTRODUCTION

Ammonia (NH_3) is one of the most widely produced chemical commodities globally, second only to sulfuric acid (H_2SO_4). In nature, it is found in the environment as a product of ammonia-producing bacteria, plants, animals, and the decomposition of organic waste. Anhydrous ammonia can be compressed under pressure into a clear liquid, and it can be stored or transported under suitable conditions.[1,2] With around 85% of its production dedicated to fertilizers for agriculture, the remaining 15% are used across various industries, such as in the manufacture of explosives and polymers, as a refrigerant, and as a reducing agent for controlling nitrogen oxide (NO_x) emissions.[3]

1.1. Importance of Ammonia in the Modern World

1.1.1. Ammonia in Agriculture

NH_3 has long been recognized as one of the most vital chemical compounds in both industrial and agricultural sectors. It serves as the main ingredient in nitrogen-based fertilizers and plays a crucial part in feeding the world's population.[1,4]

Prior to the development of synthetic nitrogen fertilizers, crop yields primarily relied on natural sources of nitrogen such as soil mineralization, the breakdown of organic matter, atmospheric deposition and biological nitrogen fixation. The scarcity of available nitrogen fertilizers has been recognized as a key factor contributing to the Malthusian Trap, a theory proposing that population growth will ultimately surpass the capacity of agricultural systems to supply sufficient food.[5]

Nitrogen gas makes up 78% of the Earth's atmosphere, but converting it into a form that can be utilized in agriculture demands a large-scale process. Direct injection of anhydrous ammonia to soil is possible. However, it is often processed into more manageable liquid or solid fertilizer forms, either applied on their own or in combination. The most commonly used solid fertilizers are ammonium nitrate, calcium nitrate and urea.[6–8]

Synthetic ammonia fertilizers are essential for global food security enabling 30-50% of agricultural crop output and are responsible for about 40% of the food supply worldwide, especially since obtaining nitrogen-based fertilizers from animal or human waste is not feasible on a larger scale due to issues with collection, transport, seasonal storage and low bioavailable nitrogen content. In addition, ammonia fertilizers help to conserve water in agriculture by increasing crop yield per unit of water used.[7,8] Due to its high nitrogen content, ammonia continues to serve as the primary compound in fertilizers essential for high global crop yields. Among the major agricultural nutrients, nitrogen supply is the most limiting factor because natural sources of nitrogen-rich minerals are far less abundant.[9]

1.1.2. Ammonia in Industries

In addition to its role in agriculture, NH_3 and its ionized form (NH_4^+) are widely used in pharmaceuticals, textiles, and chemical synthesis.[10] They also serve as precursors for the synthesis of primary amines which are required to manufacture medicines and insecticides.[11] Ammonia is used as a feedstock in the manufacture of nitric acid and acetonitrile, which are further used to produce explosives, plastics and synthetic fibers.[3] Furthermore, ammonia is utilized for antimicrobial drug production in the pharmaceutical industry as well as the production of dyes and cleaning solution.[1,12] In large-scale industrial refrigeration systems, ammonia is used as a refrigerant where it is valued for its thermodynamic efficiency and low environmental impact compared to some synthetic refrigerants.[3]

1.1.3. Ammonia as an Energy Carrier

The increasing global energy demand driven by industrial development and population growth has led to substantial greenhouse gas emissions, particularly from the combustion of conventional fossil fuels. Carbon dioxide (CO_2) is the most prevalent greenhouse gas linked to global warming, prompting urgent efforts to reduce carbon emissions. While renewable energy sources such as solar and wind are promising, their irregular availability makes energy storage a major concern. As a result, the search for alternative carbon-free fuels has intensified. Indeed, ammonia is currently a promising candidate as it is carbon-free, possesses high hydrogen density, and benefits from established production and transport infrastructure.[13]

The volumetric hydrogen density of liquid ammonia (106 kg H_2/m^3 at 300 K, 1.0 MPa) is actually higher than that of liquid hydrogen (70 kg H_2/m^3 at 20 K), making it a more efficient, cost-effective and practical hydrogen carrier.[14,15] Moreover, ammonia is easier to store as it can be compressed at room temperature or refrigerated at -30 °C. In addition, as outlined above, the transport of NH_3 benefits from an already established global distribution network, whereas hydrogen would require massive investments in pipeline and safety systems due to its volatility and low density.[16] These advantages have positioned ammonia not only as a carbon-free fuel but also as a vital part of a future hydrogen-based economy. Indeed, NH_3 has been recently accepted by global organizations as a zero-carbon molecule that can provide the required energy storage medium for renewable sources.[4,14]

Ammonia can be synthesized from abundantly available water and nitrogen and its combustion releases nitrogen, water and NO_x making its life cycle potentially CO_2 neutral. Moreover, ammonia can catalytically convert the harmful NO_x produced by its own combustion into harmless dinitrogen and water. These properties have led researchers to consider ammonia a key component of a sustainable energy economy, strengthening the case for transitioning to an "Ammonia economy".[7,14]

In evaluating ammonia as a potential clean fuel, it is essential to compare its physical and combustion properties with those of conventional fuels, particularly gasoline. Such comparison allows for a better assessment of the technical challenges and advantages associated with its adoption, especially in the context of reducing carbon emissions and transitioning to a hydrogen-based energy economy.[17] Table 1 lists the fuel properties of ammonia and other conventional fuels used worldwide in internal combustion engines such as gasoline, diesel and LPG (Liquid Petroleum Gas). This provides a comparative outlook to understand practical implications, opportunities, and limitations.[17]

Table 1: Fuel properties of NH_3 and conventional fuels

Property	Value	Interpretation
Energy Density (Liquid)	11.3 GJ m^{-3}	Lower volumetric energy compared to conventional fuels (Gasoline – 31.1 GJ m^{-3}, Diesel – 36.4 GJ m^{-3}, LPG – 86.5 GJ m^{-3})
Autoignition Temperature	651 °C	Higher than conventional fuels leading to ignition difficulties. (Gasoline – 300 °C, Diesel – 230 °C, LPG – 470 °C)
Flame Speed	0.15 m s^{-1}	Very slow compared to conventional fuels causing incomplete combustion.
Flammability Limits in Air	16.25% by volume	Requires a high concentration in air to ignite
Flash Point	−33.4 °C	Very low. Thus, exists as a liquid under moderate pressure.
Latent Heat of Vaporization	1369 kJ kg^{-1}	Very high. Thus, absorbs significant heat when evaporating.
Fuel Density (Liquid)	602.8 kg m^{-3}	Lower than conventional fuels
Storage Method	Compressed Liquid	Stored as a liquid under moderate pressure
Storage Pressure	1030 kPa	Requires pressurization at room temperature
Storage Temperature	25 °C	Can be stored as a liquid at ambient temperatures with proper pressure similar to conventional fuels.
Minimum Ignition Energy	8 MJ	Very high; harder to ignite than gasoline.

1.2. The History of Ammonia Production

1.2.1. Pre-18th Century – Early Methods of Ammonia Production

There were only two natural ways to convert atmospheric nitrogen into a usable form for living organisms before the advent of industrialization; lightning storms breaking the molecule apart by heat or enzymes of micro-organisms breaking the N≡N bonds through biological nitrogen fixation.[8,18]

Pliny the Elder provided the first known reference to ammonia, tracing it back to the Temple of Ammon in the Siwa Oasis, where camel dung was burned as fuel and ammonia-containing residues were crystallized on the walls.[10] However, these reports lack definitive historical proof since Pliny's accounts were later noted for uncertainties.[10] Ammonia was sourced from high temperature natural processes such as volcanic activity, coal seam fires and biomass combustion as well as through the dry distillation of animal matter, which was a major practice in Egypt and later in Europe.[10]

1.2.2. 18th – 19th Century – Precursor Methods for Ammonia Production

The scientific understanding of ammonia deepened in the 18th century with contributions from Joseph Black, who demonstrated the release of volatile ammonia from *sal ammoniac*. The field was further advanced through systematic studies in the 19th century that identified ammonia in air.[10]

The first experimental work involving nitrogen fixation was conducted by Joseph Priestley and Henry Cavendish prior to 1800. Their research eventually paved the way for the development of the electric arc process, which enabled the direct oxidation of nitrogen and the production of nitric acid nearly a century later. However, even with the use of low-cost hydroelectric power, the electric arc process proved to be economically inefficient.[19,20]

Although it was first isolated as a gas by Joseph Priestley in 1774 and its composition identified by Claude Louis Berthollet in 1785, it wasn't until the early 20th century that methods for producing NH_3 on an industrial scale were developed.[21]

Natural nitrogen sources including guano, crop residues and microbial nitrogen fixation (via enzymes) were insufficient to meet the demands of the world's agriculture despite their contribution to the nitrogen cycle. These techniques only provided half of the necessary nitrogen fixing at the turn of the 20th century.[9]

1.2.3. 20th Century – The Rise of the Haber-Bosch Process

Concerns about world food security over a century ago fueled the discovery and industrialization of ammonia synthesis. A foresighted speech by Sir William Crookes to the British Association for the Advancement of Science in 1898 warned of catastrophic food shortages brought on by the quick depletion of natural nitrate sources. The situation was made worse by the fact that these nitrates were not only essential for fertilizers but were also being diverted to other industries such as dyes and explosives. Crookes called on scientists to develop a synthetic method to fix nitrogen from the atmosphere so that future generations could survive.[22]

The cyanamide process was introduced in 1898 in the laboratory of Adolph Frank and Nicodem Caro in Germany, allowing nitrogen from air to be fixed into calcium cyanamide and then converted to ammonia, although this approach was highly energy-intensive.[19,21]

$$CaO_{(s)} + 3\ C_{(s)} \rightarrow CaC_{2(s)} + CO_{(g)}$$

$$CaC_{2(s)} + N_{2(g)} \rightarrow CaCN_{2(s)} + C_{(s)}$$

$$CaCN_{2(s)} + 3\ H_2O_{(l)} \rightarrow CaCO_{3(s)} + 2\ NH_{3(g)}$$

However, it was the invention and industrial scaling of the Haber-Bosch process in the early 20th century that dramatically altered the global nitrogen supply, enabling large-scale ammonia synthesis from atmospheric nitrogen and hydrogen under high temperature and pressure.[9]

In 1906, Haber made a breakthrough by synthesizing ammonia at high pressure (75 bar gauge ~ 75 atm) and temperature (1000 ºC) with an osmium catalyst, achieving a 6% ammonia concentration in the reactor, which was an important milestone for commercial viability. Recognizing that single pass conversion was insufficient, Haber developed a recycle system that continuously recovered and reintroduced unreacted gases, thus increasing the efficiency of the process. BASF bought Haber's patent and entrusted Carl Bosch with bringing the technology to full commercialization.[21]

In 1910, after testing over 2500 different catalysts, Bosch's team (which included Alwin Mittasch) replaced the expensive osmium catalyst by an iron catalyst. Alwin Mittasch played a crucial role in the advancement of ammonia synthesis by developing the iron catalyst so that the process became commercially viable (by reducing the operating temperature to below 540 ºC). This catalyst was essential in the success of the technology invented by Fritz Haber and Carl Bosch, which led to the first ammonia synthesis plant launched by BASF in 1913. The process remains the only chemical innovation to receive two Nobel prizes in Chemistry (awarded to Fritz Haber in 1918 and to Carl Bosch in 1931).[3,19,21]

The first commercial plant was established in Oppau, Germany and produced 30 metric tons of NH_3 per day. A later redesign of the reactors led to resistance to decarbonization by coating mild steel with soft iron and by including heat exchangers.[21]

The synthesis of NH_3 is thermodynamically favored at high pressures and low temperatures. However, from a kinetic perspective, temperatures above 200 ºC are required to attain meaningful conversion rates. To balance these thermodynamic and kinetic demands, the synthesis was typically carried out at moderate temperatures (400 – 450 ºC) and high pressures (150 – 250 atm) resulting in a conversion rate of 10 – 15% per pass. Eventually in 1922, the most effective catalyst was found to be a multi-component catalyst primarily consisting of an iron catalyst based on magnetite combined with small amounts of alumina, calcium oxide and potassium alkali.[23]

Following World War II, the demand for ammonia surged prompting major technological developments resulting in improved catalysts, more efficient compressor designs and integrated single train ammonia facilities, which boosted productivity capacity and energy efficiency. However, the use of fossil fuels remained unaltered. This continued dependence also poses both environmental and geopolitical challenges as ammonia production is significantly influenced by fluctuations in global energy markets.[2,21]

1.3. The Haber-Bosch Process

An estimated 180 million tons of ammonia are industrially synthesized annually worldwide, and this number is expected to increase significantly due to population growth and demands. Beyond agriculture, ammonia is gaining prominence in the energy sector as both a hydrogen carrier and a clean fuel alternative.[4,14]

Figure 1 illustrates the increasing human population over the years and their dependence on the Chilean nitrate export vs. the Haber-Bosch Process. It shows how the global population increased significantly after the Haber-Bosch process was industrialized, which highlights its role in promoting food supply through synthesis of nitrogen fertilizers. Without this development, the world population would have been 40% less than the current population.[9]

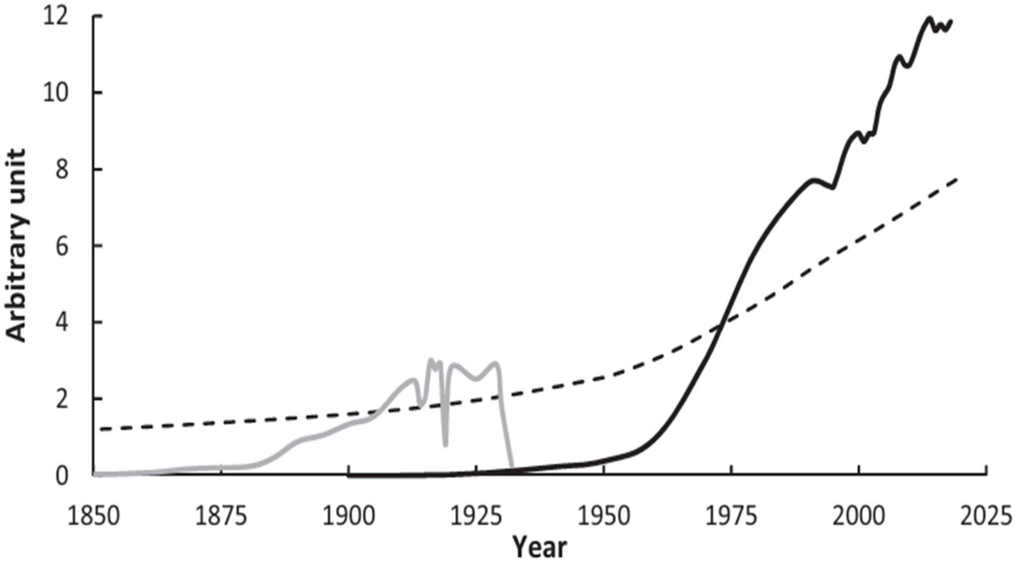


Figure 1: Dependence of the human population on the Haber–Bosch process. Taken from ref. 9 with permission from Elsevier (License No. 6146840181400). The dashed line represents the world population (x10^7 humans); the solid grey line, the annual Chilean nitrate export (x10^3 kt/year) and the solid black line shows the ammonia production by the Haber-Bosch process (x10^7 t fixed N/year).

1.3.1. The Sources and Supply of Raw Material

The nitrogen for ammonia synthesis is isolated from the atmosphere by the use of a cryogenic air separation process whereas the hydrogen can be obtained from feedstocks such as natural gas, light hydrocarbons, heavy fuel oil or coal through steam reforming or partial oxidation methods.[3,11,12]

About 70% of global ammonia production uses natural gas-based steam reforming. Other methods for producing hydrogen include the partial oxidation of heavy fuel oil or coal but these are mostly used in China, which accounts for 30% global ammonia production and 95% of global coal-based ammonia production. The choice of feedstock has a significant effect on energy consumption and carbon dioxide emissions.[24]

Figure 2 shows the Steam Reforming process which begins with feedstock preparation by mixing natural gas with a small amount of H_2, and pre-heating the mixture to 730 K. The preheated gas undergoes desulfurization, reducing all sulfur compounds to below 1 mol% in order to prevent catalyst poisoning in subsequent stages. The purified feedstock is now combined with steam in a molar ratio of 1:4 and is introduced into the primary reformer where the mixture passes over a nickel-based catalyst enclosed in radiation-heated channels. There, the feedstock is partially reformed into a synthesis gas consisting of hydrogen, carbon monoxide and carbon dioxide (~ 66% methane conversion). This syngas is directed to a secondary reformer to react with a controlled volume of preheated and compressed air to further reform the gas.[25]

The process continues with the water-gas shift reaction, which converts the carbon monoxide into additional hydrogen and more readily separable carbon dioxide ($CO_{(g)} + H_2O_{(g)} \leftrightharpoons CO_{2(g)} + H_{2(g)}$). The carbon dioxide is then effectively removed from the main gas stream under high pressure, commonly via a solvent-based (generally monoethanolamine) absorption process. Finally a methanation step is employed to eliminate residual carbon oxides, reducing their concentration to below 10 ppm, thus producing high-purity hydrogen.[25,26]

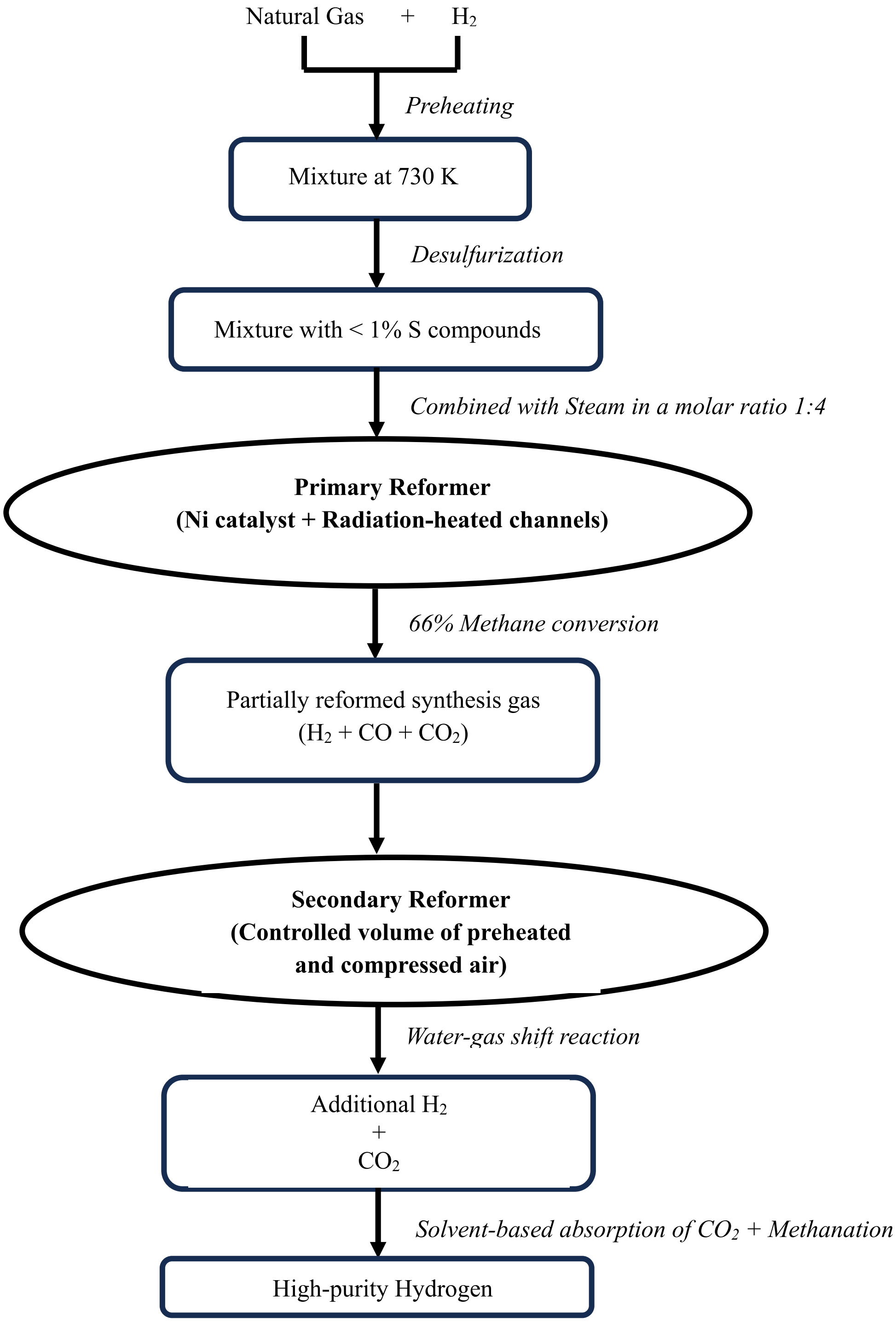


Figure 2: Flowchart of the Steam Methane Reforming Process.

1.3.2. The Mechanism and Operation

The nitrogen and hydrogen gases are introduced into a reactor containing an iron-based catalyst, often promoted with potassium and aluminium oxides, which enhance the rate of ammonia formation.[27]

$$3\ H_{2\,(g)} + N_{2(g)} \rightleftharpoons\ 2\ NH_{3(g)}$$

$$H^{0}_{298} = -\,92.4\ \text{kJ mol}^{-1}$$

$$\Delta G^{0}_{298} = -\,32.8\ \text{kJ mol}^{-1}$$ [28]

However, due to the strong N≡N triple bond in N_2 (with a bond dissociation energy of 941 kJ/ mol) the reaction requires a significant amount of activation energy. Inside the reactor, multiple circulations of gases are often required because the reaction is equilibrium-limited and the unreacted gases are recycled.[29,30]

Although thermodynamically favorable at low temperatures, high temperatures are needed to achieve practical reaction rates which leads to a compromise between yield and rate. The catalyst employed in modern Haber-Bosch synthesis usually deliver conversion rates of around 10-15% when subjected to high pressure (> 100 atm) and high temperature (425-450 ºC). The process design balances these factors by using high pressure to shift the equilibrium towards ammonia formation and implementing gas recycling systems to improve overall efficiency.[9,31,32]

CHAPTER 2 – CHALLENGES OF CONVENTIONAL AMMONIA PRODUCTION & EMERGING ALTERNATIVES

2.1. Limitations of the Haber-Bosch Process

While the Haber-Bosch process is highly efficient and globally entrenched, with the shift towards carbon neutrality and the utmost need to decarbonize industrial sectors, it is considered one of the most energy- and carbon-intensive industrial operations.

Fossil fuel dependence

Roughly 70% of worldwide ammonia production depends on the hydrogen gas produced through steam reforming methods requiring fossil fuels, particularly natural gas. This reliance leads to substantial CO_2 emissions and fossil energy consumption.[24,33]

Carbon footprint

Approximately 600 kg of natural gas are required for hydrogen production via steam methane reforming to produce 1000 kg of ammonia, contributing to over 670 million tons of fossil CO_2 emissions annually. This accounts for nearly 2.5% of all fossil fuel-based CO_2 emissions worldwide and 1.8% of global CO_2 emissions.[4,9]

Climate challenges

The emission of CO_2 from the synthesis of ammonia has also grown to be a significant problem in the current setting of accelerating climate change due to it being a potent greenhouse gas. If current emission rates persist, projections indicate that the global temperatures would rise by 1-1.5 ^{o}C by 2050, highlighting the necessity of implementing low-carbon industrial solutions.[14]

Energy requirements

The energy intensity of the Haber-Bosch process is largely due to hydrogen production. Even if a revolutionary catalyst enabled ammonia synthesis at room temperature and atmospheric pressure, the overall energy savings would be marginal because the hydrogen production would still dominate the energy demand.[4]

Limitations of the catalyst

The core limitation of the conventional catalyst is its poor performance under ambient conditions. At low temperatures and pressures, important reaction intermediates such as adsorbed nitrogen (N), imide (NH) and amide (NH_2) bind excessively to the catalyst surface, especially on metals such as ruthenium, effectively saturating active sites and stopping intended reactions. Although raising the temperature aids in the desorption of these tightly bound species, it also modifies the whole free energy balance making the reaction non–spontaneous unless the pressure is also raised. These intrinsic catalytic limitations highlight the need for novel materials capable of enabling ammonia production in more sustainable and milder environments.[34] Despite these limitations, the process currently supports a global ammonia market that exceeds 180 million metric tons per year, underlining the urgent need to develop greener alternatives that maintain efficiency while reducing environmental impact.[14,35]

2.2. <u>The Need for Sustainable Ammonia</u>

The need for sustainable ammonia arises from the high energy consumption and significant CO_2 emissions associated with conventional ammonia production, which relies heavily on fossil fuels such as natural gas and coal. The Haber–Bosch process coupled with steam reforming emits large quantities of CO_2, making ammonia one of the most carbon-intensive chemicals.[36]

Furthermore, the reliance on nitrogen fertilizers creates a direct connection between food supply and fossil fuel consumption, along with the high carbon emissions. This dependence results in food production systems that are unsustainable and vulnerable to price instability as rising fossil fuel costs can cause sharp increases in food prices.[6]

Researchers have been investigating more energy-efficient catalytic systems that can function in milder environments in order to overcome the issues arising with the Haber–Bosch process. As an example, ruthenium-based catalysts exhibit potential but are costly due to their limited availability. Novel metal catalysts based on molybdenum that have accomplished nitrogen fixation at room temperature and atmospheric pressure, are now being developed to replicate biological nitrogenase systems. Nonetheless, these efforts are still in their experimental stage.[11]

In contrast to conventional techniques, green ammonia synthesis reduces the need for fossil fuels significantly, thus lowering emissions and gaining independence from an unstable world energy market.[2] In addition, green ammonia serves a dual purpose; it can be directly used as a fuel or as a hydrogen carrier. Its potential use in power generation, fuel cells and combustion engines further elevates its role in transitioning towards a sustainable energy future. As governments and businesses prioritize the transition to clean energy and carbon neutrality, green ammonia is gaining significant attention as a clean, storable and globally tradable energy carrier that aligns with the long-term goals of decarbonization and sustainable development.[2,37]

2.3. Common Goals of Alternatives

The Haber-Bosch process being one of the largest energy-demanding industrial processes, with extreme conditions of temperature and pressure achieves conversion rates of only 10–15% per pass, creating a necessity for recycling loops that further increase the energy demand. Alternative production pathways are now being developed to enable ammonia synthesis capable of operating under milder conditions by developing catalysts and electrochemical systems that are compatible with renewable energy sources.[31] As mentioned earlier, conventional steam methane reforming relies heavily on fossil fuels and releases substantial amounts of CO_2 as a byproduct. By replacing fossil-based hydrogen with renewable sources, the alternative methods contribute directly to global emission reduction.[38]

Finally, nitrogen recovered from waste streams or the atmosphere can be efficiently cycled back into ammonia reducing the need for the fossil-based feedstocks while simultaneously addressing ecological issues such as fertilizer runoff polluting waterways and contributing to nitrogen circularity by recovering nitrogen from waste and converting it into fertilizer.[4,18]

2.4. Emerging Pathways for Sustainable Ammonia Synthesis

Driven by the urgent need to decarbonize ammonia synthesis in line with climate commitments such as the Paris Agreement, researchers have started to develop greener alternatives that use milder conditions and integrate renewable energy to overcome the energy and pressure demands of the Haber-Bosch process. Traditional brown ammonia produced from coal gasification is carbon intensive whereas the green ammonia produced sustainably offers near zero emission.[39]

Emerging routes include electrochemical and photochemical processes, chemical looping and biochemical pathways, although significant advances are still required to achieve practical efficiencies. Given the intrinsic limitations of N≡N bond activation, broader nitrogen management is also critical, considering not only N_2 reduction, but also how different nitrogen compounds can be converted and recycled within the nitrogen cycle. Recent progress spans from catalyst design incorporating technical performance such as efficiency, stability, and energy demand to economic feasibility (overall process costs). It is also important to assess whether these emerging pathways can realistically compete with the conventional Haber-Bosch process.[40,41]

In the following chapters five promising new pathways will be explored: electrocatalytic nitrate reduction (which simultaneously can treat wastewater and generate ammonia), direct electrochemical nitrogen reduction powered by renewable electricity, the renewable-powered Haber–Bosch process using green hydrogen instead of fossil-derived hydrogen, photocatalytic solar-driven ammonia production that mimics photosynthesis to fix nitrogen, and biological nitrogen fixation (leveraging natural or engineered microbes). Together these approaches aim to reduce energy demands, promote renewable resource integration and circular nitrogen management and offer feasible solutions for transitioning ammonia production towards a sustainable future.[40,42]

CHAPTER 3 – ELECTROCATALYTIC NITRATE REDUCTION

Electrocatalytic Nitrate Reduction (ENR) is becoming a viable energy-efficient alternative to the energy-intensive Haber–Bosch process. Unlike N_2, nitrate has a higher solubility and a smaller dissociation energy (of the N=O bond), thus enabling a more effective catalytic conversion under ambient conditions.[42]

The process can be powered by renewable electricity, providing a carbon-neutral pathway while also removing nitrate pollution from water sources, and therefore contributing to restore the global nitrogen cycle.[43] Indeed, nitrate pollution in water bodies poses severe environmental and health threats. ENR has emerged as a potential dual-purpose solution, enabling both nitrate removal from water and green ammonia synthesis.[42,44]

The ENR mechanism typically begins with the adsorption process followed by the activation of the nitrate ions on the surface of a catalyst and proceeds with multi-electron and -proton transfer steps. Nitrite (NO_2^-) is a crucial intermediate formed in the process, which is further reduced into NH_3 via adsorbed nitric oxide (NO) or, in some cases, N_2.[43]

3.1. Catalyst Design

3.1.1. Transition Metal–Based Catalysts

Transition metal oxides based on Cu, Ni and Co have been widely investigated for the ENR due to their favorable electrocatalytic properties. In particular, Ni and Co-based catalysts have demonstrated high activity while Cu-based electrocatalysts are extensively explored for their ability to selectively reduce nitrate to ammonia via favorable adsorption of nitrate and intermediates.[45]

Cu/CoP/NF (Copper/ Cobalt phosphide/ Nickel foam) catalyst: This composite cathode coupled with an Ir-Ru/Ti anode enables efficient electrocatalytic nitrate reduction in surface water. Cu/CoP enhances the active sites and electron transfer, achieving nearly a complete nitrate removal with NH_4^+ being the main product (selectivity of 94.5% in 180 minutes, low selectivity for N_2). However, Cl^- addition promotes active chlorine (Cl_2/HOCl) at the Ir-Ru/Ti anode, which oxidizes NH_4^+ (formed at the Cu/CoP/NF cathode) to N_2. This paired reduction-oxidation process raises N_2 selectivity to 98.8%. Thus, this process achieves 94% nitrate and total nitrogen removal over multiple cycles, meeting water quality standards in real samples.[46]

Cu (111) nanosheets: This system offers a sustainable route for ammonia synthesis benefiting from the high solubility and availability of nitrate sources. The facet-dependent catalyst achieves an exceptional NH_3 formation rate of 390.1 $\mu g\ mg^{-1}$ Cu h^{-1} with 99.7% Faradaic Efficiency (FE) at -0.15 V vs. RHE (Reversible Hydrogen Electrode). In addition, the hydrogen evolution reaction (HER) is suppressed and nitrate-to-nitrite conversion is accelerated. Structural sensitivity is confirmed by the superior performance of Cu (111) compared to Cu (100), highlighting ENR as an efficient approach to both ammonia production and nitrate remediation.[47]

Other than Cu, a variety of catalyst engineering strategies have been explored to improve the performance. For example, a Ni-Mo-P/TiO_2 nanoribbon array catalyst delivers 95.6% FE with a high yield of NH_3 (16,125 $\mu g\ h^{-1}\ cm^{-2}$) for the electrocatalytic nitrite reduction in alkaline media.[48] Its superior performance arises from the synergistic Ni-Mo-P/TiO_2 heterojunction and the amorphous Ni-Mo-P structure facilitating proton transfer and N=O bond cleavage with an excellent stability over 12 hours.[48]

Oxygen-doped strained Ru nanoclusters: This system demonstrates exceptional performance in nitrate reduction by combining high activity with long term stability. The tensile strain on the Ru surface raises the energy barrier for H–H pairing, thereby suppressing the competing HER while also promoting nitrite hydrogenation. As a result, this catalyst system displays nearly 100% ammonia selectivity (98-99%) with an ammonia formation rate of 20,000 μg h^{-1} mg^{-1} for over 100 hours. Even at current densities above 120 mA cm^{-2}, the process is efficient, making the Ru nanocluster one of the most efficient electrocatalysts reported.[43]

Single atom catalysts (SACs): SACs such as Fe-N-C (Single Fe atoms anchored on N-doped carbon) and Cu-N-C (Cu atoms coordinated with N in a carbon network) provide high atomic utilization and uniform active sites. These properties are effective at suppressing HER while simultaneously enhancing the activation of nitrates. Possessing excellent long term stability, they achieve almost 95% FE and an ammonia production rate of up to 16,000 μg h^{-1} mg^{-1}.[43]

3.1.2. Non-Metal and Noble Metal Catalysts

Fluorine-doped carbon (FC): FC is a non-metallic catalyst prepared from waste material such as cigarette filters, where the fluorine doping creates positively charged carbon sites that enhance nitrate absorption, suppress the HER and lower the energy barrier for the rate-limiting step (conversion of NO to NOH). It delivers a FE of 20% and an ammonia production rate of 23.8 mmol h^{-1} g^{-1} with the catalyst remaining stable for 10 hours.[49]

Ag nanoarray using NiO nanosheets on Carbon Cloth (Ag@NiO/CC): This material efficiently catalyzes nitrate reduction to ammonia in 0.1 M NaOH and achieves a FE of 75.8% at – 0.5 V. The yield of NH_3 is 2,290 μg h^{-1} cm^{-2} (or 22,900 μg h^{-1} $mgAg^{-1}$) even though NO_3^- reduction is slower than that of NO_2^- due to the higher N=O bond energy.[50]

3.1.3. Bimetallic Phosphides/Oxides and Heterojunctions

By combining Co^{2+}/Co^{3+} redox cycling with indirect hydrogen atom pathways, NiCoP/NF electrodes achieve 97.7% nitrate removal and 95.4% ammonia selectivity under mild conditions (pH 7; 2 mA cm^{-2}). Mechanistic studies indicate a dominant direct reduction via Co^{2+}/ Co^{3+} redox cycling alongside minor atomic hydrogen-mediated indirect reduction, highlighting the synergistic advantage of bimetallic phosphides for selective and sustainable nitrate-to-ammonia conversion.[51]

Figure 3 describes how the NiCoP/NF catalyst reduces nitrate to ammonia through two linked mechanisms. First, nitrate ions bind to Ni and Co sites, while nearby phosphorus atoms attract protons generated from water dissociation. In the direct pathway, cobalt actively transfers electrons to nitrate and its intermediates (cycling between Co^{2+} and Co^{3+}), converting them to ammonia. In the indirect pathway, hydrogen atoms (H*) formed on the catalyst surface react with nitrate species to form NH_4^+. Together, these steps explain the catalyst’s high selectivity and efficiency for ammonia production.[51]

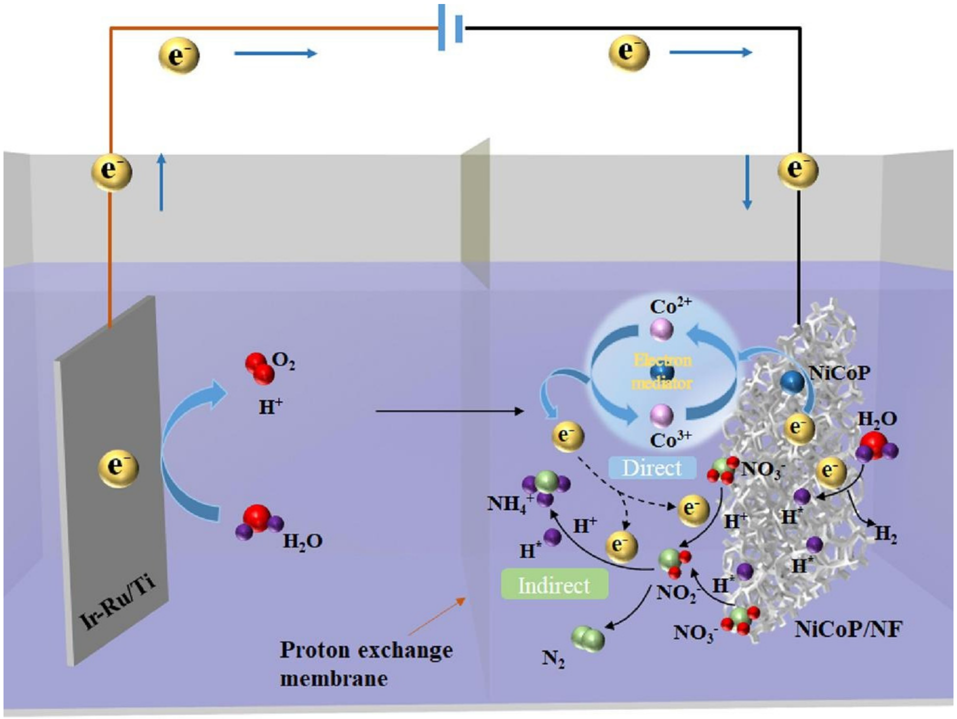


Figure 3: The mechanism of electrochemical NO_3^- reduction using a NiCoP/NF cathode. Taken from ref. 51 with permission from Elsevier (License No. 6147161223689).

<u>CoP/TiO_2 p–n heterojunction:</u> This interface engineering strategy enhances charge transfer, lowers reaction barriers (0.73 eV) and suppresses side reactions, achieving 95% FE and a high yield of 500 μmol h^{-1} cm^{-2} NH_3. The minimal by-product formation ensures its high selectivity towards NH_3.[52]

Figure 4 shows how electrons are redistributed at the interface when CoP (p-type) and TiO_2 (n-type) from a p-n junction. The redistribution of electron density indicates strong interfacial electronic interaction and formation of a built-in electric field that facilitates charge transfer between CoP and TiO_2. Such charge modulation enhances the electronic conductivity and optimizes the adsorption energy of nitrate intermediates, thereby promoting NO_3^- reduction.[52]

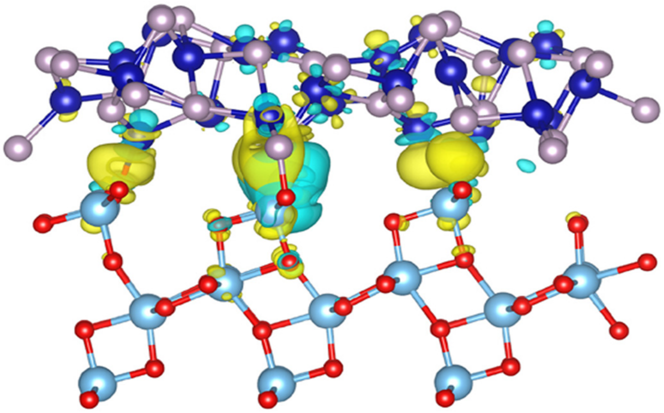


Figure 4: Charge density difference plot of CoP/TiO_2. Taken from ref. 52 with permission from Elsevier (License No. 6147400931940). Yellow regions represent areas of electron accumulation and cyan regions show electron depletion. Dark blue: Co; Mauve: P; Red: O; and Light blue; Ti.

<u>$ZnCo_2O_4$ nanosheet array on Carbon Cloth ($ZnCo_2O_4$/CC):</u> This 3D catalyst inhibits HER and facilitates an efficient NO_3^- transport, achieving a 98.33% FE at -0.6 V. At a more negative potential of -0.8 V, it delivers a high NH_3 yield of 634.74 µmol h^{-1} cm^{-2}.[53]

Despite all the aforementioned catalyst developments, difficulties still remain as far as the competing HER processes are concerned. HER diverts the electrons from nitrate reduction lowering ammonia yields. In addition, byproducts such as N_2 reduce selectivity. Catalyst corrosion is an issue particularly in Cu-based systems, which hinders long-term operation and limits mass transportation at high current densities. To overcome these challenges and for a better understanding of the reaction pathways, in-situ characterization techniques are essential for tracking reaction intermediates and guiding catalyst design for scalable ENR-based ammonia production.[42,43]

3.2. Reactions and Mechanisms

3.2.1. Key Steps and Intermediates

The ENR pathway typically proceeds in multiple steps as follows. Nitrate ions first adsorb onto the catalyst surface, facilitated by active sites on Cu, Ni, alloys or defect-rich metal oxides (oxygen vacancies and nanostructured surfaces) to enhance electron transfer.[47,54] Nitrate is then reduced to nitrite in the rate-determining step, which is accelerated by Cu (111) facets, oxygen-doped metals or alloyed surfaces which reduce binding energies and suppress the competing HER.[47,54]

Nitrite is then further reduced via the formation of an adsorbed nitric oxide (NO*) intermediate. The NO* intermediate is widely recognized as a branching point in the reaction pathway, as its subsequent transformation strongly depends on catalyst properties, reaction conditions and surface binding energies.[43] The reduction to NH_3 occurs on catalysts such as Cu-based nanosheets, Fe- or Cu-based single atom catalyst or oxygen-doped Ru nanoclusters achieving high selectivity and near 100% FE in some cases. Formation of N_2 may compete depending on the HER and adsorption energies.[43,47]

However, in Cl^--containing systems, NH_4^+ produced from NO_2^- reduction can be oxidized to N_2 via anodically generated active chlorine, increasing N_2 selectivity (representing a competing oxidation route that lowers NH_4^+ selectivity) despite maintaining overall nitrate removal.[46]

3.2.2. Competing Reactions

HER is a major competing reaction in nitrate reduction, diverting electrons from NH_3 formation. HER is effectively suppressed in Cu (111) nanosheets by facet engineering and low overpotential, achieving a FE 99.7% for ammonia.[47] In fluorine-doped carbon (FC), HER is partially suppressed through F-doping as positively charged sites are created that favor nitrate adsorption. This lowers the energy barrier for nitrate hydrogenation (NO → NOH), but limits the FE to 20%. In Cu/CoP/NF, HER is minor because hydrogen generated on CoP participates in nitrate reduction rather than forming H_2, thus enabling maximum nitrate removal.[46,49]

N_2 formation competes with NH_3 formation by consuming NH_4^+, hence, reducing ammonia yield. Using Cu/CoP/NF, active chlorine is generated at the anode, which oxidizes NH_4^+ to N_2, thus increasing N_2 selectivity to 98.8% while maintaining maximum nitrate removal.[46]

3.2.3. Electrolyte Composition and pH

Studies across different systems demonstrate that electrolyte composition plays a crucial role in determining product selectivity and efficiency in nitrate and nitrite reduction. The Cu/CoP/NF system shows how neutral electrolytes ($pH \approx 7$) containing Cl^- ions can alter the selectivity. Without Cl^-, NH_4^+ dominates, but with Cl^-, active chlorine generated at the anode oxidizes NH_4^+ to N_2. This highlights the potential of neutral electrolyte systems containing additives for water purification and nitrogen gas release.[46]

In strongly alkaline electrolytes (such as 0.1 M NaOH used with the Ag@NiO/CC system) ammonia production is highly favored. The alkaline environment provides abundant OH^- ions to accelerate multi-electron reduction steps from nitrite to ammonia while suppressing the competing HER as supported by both the high FE and by Density Functional Theory (DFT) calculations.[50]

Similarly, the Ni-Mo-P/TiO_2 nanoribbon array uses alkaline conditions alongside a heterojunction interface to achieve high ammonia yields. These cases underscore the synergy between alkaline electrolytes, catalyst structure and system design in directing reactions towards efficient NH_3 synthesis.[48]

In contrast, Nafion-based membrane systems behave very differently. Operating under acidic conditions, these polymer electrolyte systems enable simplified reactor designs (with simpler operation) and achieve promising ammonia production rates (1.13×10^{-8} mol cm^{-2} s^{-1} with 90% efficiency). However, they suffer long-term durability challenges due to ammonium ion exchange, which reduces membrane conductivity. While humidification mitigates some of these effects, membrane stability remains a limitation for the practical use of these systems.[55]

3.2.4. Direct vs. Indirect Reduction

The ENR can proceed via two pathways: Direct reduction through electron transfer from the electrode surface and indirect reduction mediated by electrogenerated atomic hydrogen (H*).[46,51]

Table 2 shows the direct and indirect reductions observed in certain electrocatalytic systems and their contribution to the reduction process.

Table 2: Direct vs. indirect nitrate reduction in electrocatalytic systems

Electrocatalytic System	Direct Reduction	Indirect Reduction
Cu/CoP/NF[46]	In this system, Cu nanoparticles facilitate the direct conversion of nitrate to nitrite. This pathway contributes significantly alongside indirect processes making the system a combination of both mechanisms.	Indirect pathways are significant in this system. CoP-generated H* reduces NO_2^- to ammonium (NH_4^+), and, in the presence of Cl^-, anodically produced active chlorine further oxidizes NH_4^+ to N_2, adding an additional indirect step.
NiCoP/NF[51]	Direct reduction is the dominant mechanism in this system. Electrons are transferred via Co^{2+}/Co^{3+} redox cycling to reduce NO_3^- directly to ammonia.	H*-mediated indirect reduction of intermediates such as NO_2^- contributes only minimally.
CoP/TiO_2 nanoarray[52]	The p–n heterojunction promotes electron transfer from CoP to adsorbed NO_3^-, lowering the energy barrier for NH_3 formation. Direct electron transfer is therefore the primary pathway with only minor contribution from indirect processes.	Indirect H*-assisted reduction plays only a minor role.

3.3. Environmental Applications

Electrocatalytic nitrate reduction offers dual environmental benefits: efficient water purification and sustainable resource recovery. Recent studies highlight different strategies to achieve these goals, demonstrating both practical applicability and alignment with circular economy principles.

Water treatment

The Cu/CoP/NF system demonstrates strong potential for water remediation, achieving near complete nitrate removal and product selectivity depending on the amount of chloride present.[46]

It treats surface water effectively, meeting China's class III-IV standards with >94% total nitrogen removal. It also maintains high performance over multiple cycles, highlighting its suitability for practical large-scale wastewater treatment.[46]

Waste valorization

The FC catalyst (obtained from waste-derived materials such as pyrolyzed cigarette filters saturated with polytetrafluoroethylene (PTFE)) can be used for sustainable ammonia production. By converting nitrate into ammonia, it not only purifies water but also supports resource recovery. Its metal-free design, high selectivity and operational stability make it attractive for environmentally friendly applications.[49]

CHAPTER 4 – ELECTROCHEMICAL NITROGEN REDUCTION

In the search for a more sustainable ammonia economy, the electrochemical Nitrogen Reduction Reaction (NRR) has emerged as a promising alternative to the Haber-Bosch process. Unlike the conventional NH_3 synthesis, NRR aims to synthesize ammonia from nitrogen gas and water using renewable electricity, operating at ambient or moderate conditions of temperatures and pressure.[29,55,56] This approach potentially eliminates the carbon footprint associated with H_2 production, bypassing the need for fossil fuels and aligning with the global efforts towards decarbonization.[57]

NRR mimics biological nitrogen fixation, which is carried out by the nitrogenase enzymes. It is achieved at ambient pressure using protons and electrons supplied electrochemically (ideally using renewable energy sources).[29,56,57] The first successful demonstration of NH_3 synthesis under mild conditions was reported in 1998 by Marmellos and Stoukides, who employed a proton-conducting oxide electrolyte ($SrCe_{0.95}Yb_{0.05}O_{3-\delta}$). Their work proved that NH_3 could be produced under atmospheric conditions, laying the foundation for future electrochemical approaches.[58,59]

4.1. Principles of Electrochemical NRR

4.1.1. Core Concept

The NRR process relies on an electrochemical cell that performs N_2 reduction with proton transport. At the anode, either hydrogen or water is oxidized to generate H^+ and electrons. These protons migrate through the electrolyte and reach the cathode where they react with N_2 molecules adsorbed onto a catalyst surface (with uptake of electrons) forming NH_3. The appeal of this process lies in its operational simplicity and compatibility with renewable energy sources. Unlike the

Haber-Bosch process, which requires purified H_2 gas (typically derived from steam reforming of methane), NRR utilizes water as the proton source, which significantly simplifies the process and avoids fossil fuel-based CO_2 emissions.[55,58]

4.1.2. Electrochemical Cell Operation

Figure 5 shows a schematic diagram representing the operating principle of an NRR cell. At the anode, H_2 gas is supplied and oxidized, generating protons (H^+) and electrons (e^-). If water is used as the proton source, it undergoes electrolysis to form oxygen and protons.

The H^+ generated at the anode then migrates through a solid proton-conducting electrolyte membrane. At the cathode, the H^+ traveling through the electrolyte combines with nitrogen molecules (N_2) and electrons from the external circuit to form NH_3. The outlet stream contains the produced NH_3 along with unreacted H_2 and N_2.[55]

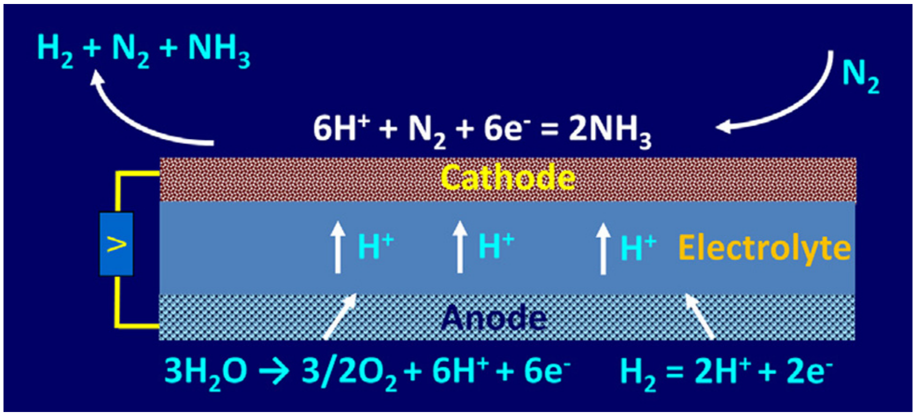


Figure 5: Electrochemical route of ammonia synthesis based on a proton-conducting solid electrolyte. Taken from ref. 55 with permission from Elsevier (License No. 6147401386631).

4.2. Mechanistic Pathways

4.2.1. Primary Pathways

NRR can proceed via different mechanistic routes on catalytic surfaces. The reaction is believed to proceed through two primary mechanistic pathways.

1. Dissociative mechanism

The N≡N triple bond is cleaved before hydrogenation, a step that requires high energy input and is often considered impractical under ambient electrochemical conditions. It forms two N atoms (*N) which are then sequentially hydrogenated to form *NH, *NH_2 and finally NH_3. This mechanism is typically favored on surfaces with strong nitrogen binding energies and at higher temperatures.[29,37,56]

2. Associative mechanism

This is the more common pathway. It involves gradual hydrogenation of one nitrogen atom before N≡N bond cleavage, a feature that is more consistent with the low temperature operation.[37,56,57]

The associative pathway is further divided into three pathways (distal, alternating and enzymatic; see Figure 6). In the distal pathway, one N atom is fully hydrogenated before the other. The hydrogenation occurs on the terminal nitrogen atom first, eventually releasing the first NH_3 molecule and leaving a second *N atom to be hydrogenated. In the alternating pathway, the N_2 molecules are adsorbed in an end-on configuration. This pathway hydrogenates both N atoms in an alternate fashion until NH_3 is formed. In the enzymatic pathway, which mimics nitrogenase with side-on N_2 binding, the N_2 molecule binds parallel to the catalyst surface, allowing simultaneous interaction with multiple active sites.[29,37,56,57]

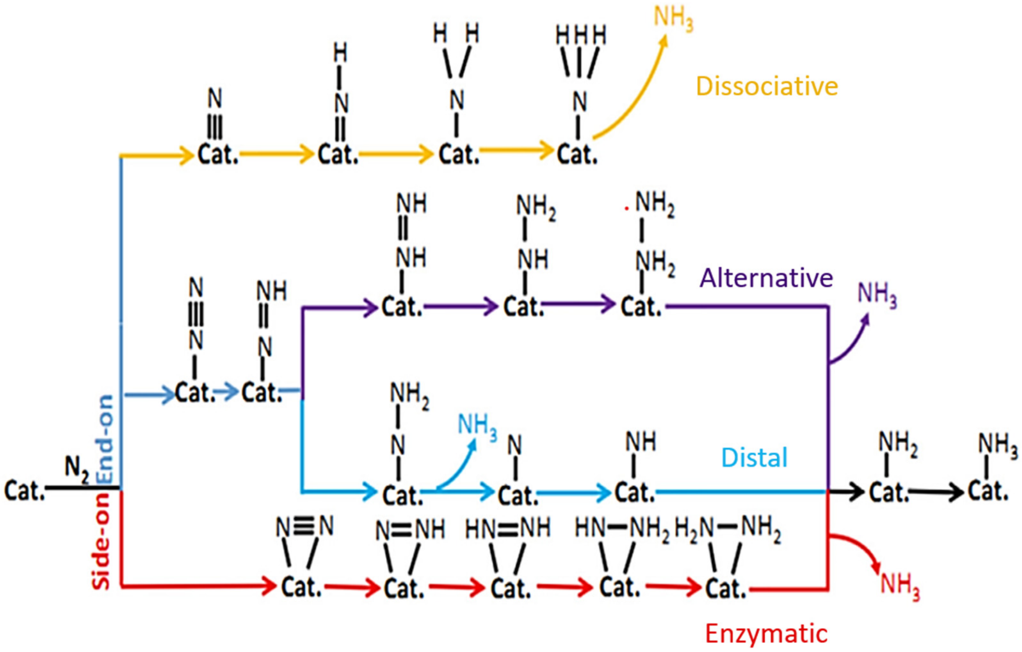


Figure 6: **NRR reaction pathways. Modified from ref. 57 with permission from Elsevier (License No. 6151340806755).**

4.2.2. Mechanistic Variants

Beyond the above-mentioned classical routes, recent studies have introduced new mechanistic variants.

Mars-van Krevelen (MvK) mechanism

The MvK mechanism, proposed for transition metal nitrides, involves lattice N atoms within the catalyst structures. The N_2 is reduced into NH_3 leaving back N vacancies on the catalyst surface. These vacancies then act as active sites for further N adsorption, enabling regeneration of the catalyst. The pathway bypasses the high barrier of N≡N bond cleavage by temporarily incorporating N into the lattice before hydrogenation and release of NH_3 occurs. However, vacancies can be filled also by competing species such as H^+, O^{2-} or OH^-, which can hinder catalyst regeneration.[37,57,60]

Surface hydrogenation

This pathway occurs with noble metal catalysts. Unlike the associative or dissociative pathways, this mechanism begins with the protons being reduced to surface hydrogen atoms (H*). These H* species activate N_2 and drive its stepwise conversion to NH_3. This route differs from the others due to surface hydrogen acting as the main driver of NRR activity under mild conditions.[60]

4.3. NRR Electrocatalysts

4.3.1. Catalyst Design

Electrocatalysts are central in achieving efficient electrochemical NRR under mild conditions as they mediate nitrogen adsorption, activation and hydrogenation, and ideally suppress the HER. An ideal catalyst must be strong enough to activate the stable N_2 molecule but also weak enough to allow the desorption of the NH_3 product, thus avoiding poisoning of the active sites.[37]

Several factors shape catalytic activity including particle size, electronic structure, coordination environment and crystal orientation. For instance, reducing catalyst size exposes more active sites. As such, smaller catalysts such as quantum dots and Single-Atom Catalysts (SACs) significantly maximize active sites and enhance reactivity.[37]

Furthermore, heteroatom doping (Fe, B) and heterostructure formation alter the electronic behavior of active sites or create new active centers for N_2 adsorption and activation. In addition, amorphous structures and defect engineering can provide unsaturated sites and lower energy barriers by introducing vacancies (O, S or N) that further enhance adsorption and activation of N_2. Finally, the orientation of crystal planes can strongly influence adsorption behavior and catalytic activity.[37]

4.3.2. Catalyst Material

Electrocatalyst innovation is the most active area in NRR research as catalyst surfaces control nitrogen adsorption, activation and HER suppression.

Table 3 shows various classes of catalysts that have been explored for electrochemical NRR, each offering advantages as well as disadvantages. Transition metal catalysts and SACs provide high activity and selectivity, but require more drastic operating conditions (e.g., high temperature). Main group, perovskite, oxide and defect-engineered catalysts show efficient synthesis under mild conditions, but stability and efficiency remain challenging. Emerging 2D materials offer large surface areas and electronic tunability. However, the performance of these materials is still being evaluated.

Table 3: Catalyst classes for Electrochemical NRR

Catalyst Type	Examples	Catalytic performance	Advantages	Disadvantages	Ref
Transition metal catalysts	Ru, Mo, Fe, Ti, Zr, Y, VN, CrN, NbN, Ru-doped titanates	Transition-metal nitrides showed FE > 75% Ru-doped titanates showed FE of 5.9% at 500 °C, 1.2 V	High catalytic activity (Transition-metal nitrides) Strong N_2 binding Nitrides show high FE	High operating temperature Limited FE in certain systems	[29,56,61]
Main group element catalysts	B, Bi, Al, Si, Pb, Lithium mediated system	Lithium-mediated systems show reliable N activation under ambient conditions.	Suppresses HER due to weak H adsorption Effective under mild conditions	Limited stability Li mediated systems need careful handling	[43,62]
Perovskites and oxide catalysts	Cobalt containing perovskites, Oxygen vacancy-engineered perovskites	Ammonia formation doubled vs. cobalt free with FE 0.20%	Vacancy engineering improves activity Perovskites are tunable	Instability under reducing conditions Very low FE	[63]

Table 3 (Continued)

Defect engineered catalysts	Vacancies in O, N, S	Improved N adsorption/activation	Creates active sites Efficient electron transfer	Complex synthesis Stability issues	[64,65]
Single-Atom Catalysts (SACs)	Isolated single atoms Ru, Fe, Mo Catalyst	Enhanced NRR Suppressed HER	Maximizes atom utilization High selectivity HER suppression	Challenging synthesis High cost Stability concerns	[29,60,64]
Two-dimensional (2D) materials	MXenes, MoS_2, Boron-based nanosheets	Large surface area Tunable properties	High surface area Electronic tunability Scalable 2D structures	Still under exploration Limited efficiency data available	[29,37]

4.4. Electrolyte Systems

Electrolytes are central to NRR performance, as they provide the medium for proton transport, influence nitrogen solubility and shape competition with HER.

1. Aqueous systems

These are the most commonly studied but face the most severe challenges. The HER is overwhelmingly dominant in water, drastically reducing FE, which is often reported to be less than 10%.[29,56]

2. Liquid electrolytes

This includes organic solvents such as tetrahydrofuran and ethanol, which achieve current efficiencies of 5-8% under ambient conditions, although performance improves under high nitrogen pressure, with reports of 58% efficiency at 50 atm and 50 ºC using iron cathodes.[55] Molten salt systems such as LiCl-KCl-CsCl eutectics containing dissolved Li_3N exhibit higher efficiencies, reaching 72% at 400 ºC with porous nickel electrodes.[55]

3. Solid electrolytes

Solid electrolytes such as perovskites, fluorites and pyrochlores, which have an ordered fluorite structure (sometimes referred to as fluorite superstructures), provide structural stability. They occasionally achieve conversion efficiencies above 50% but are limited by low current densities.[55,56] Polymer electrolyte membranes (PEM), particularly Nafion-based membranes, have demonstrated high rates up to 1.13×10^{-8} mol cm^{-2} s^{-1}, but stability issues remain a concern due to NH_3-induced membrane degradation.[55,56]

4. Ionic liquids and non-aqueous systems

Compared to non-aqueous solvents (molecular solvents), ionic liquids have good electrical conductivities and strong electrostatic fields. These systems are being investigated as promising electrolytic media for improving both activity and selectivity. They provide high nitrogen solubility and suppress HER by limiting proton availability, thus leading to some of the highest reported efficiencies (Up to 60% in the hydrophobic ionic liquid trihexyl(tetradecyl) phosphonium tris(pentafluoroethyl) trifluorophosphate, $[P_{6,6,6,14}]^+[eFAP]^-$). Their ionic microenvironments and ability to enhance N_2 solubility make them attractive for the further development of nitrogen fixation methods under ambient conditions.[37,57,66]

4.5. Cell Configuration

The design of electrochemical reactor cells plays a key role in the NRR. Figure 7 illustrates the four categories of cell configuration.

Back-to-back cells: This configuration consist of two porous electrodes separated by a dense membrane such as Nafion or an anion exchange membrane (AEM). This solid electrolyte system enables controlled proton supply, which helps suppress the HER. Protons and electrons generated in the liquid chamber act on the solid layers to convert N_2 to NH_3.

PEM-type cells: These operate similar to the back-to-back cells but include a reference electrode to stabilize the cathode potential. Since there is no water at the cathode, both back-to-back and PEM-type cells can avoid the HER.

Single-chamber cells: In contrast to back-to-back and PEM-type cells, the single-chamber cell is filled with electrolyte and the catalyst is in direct contact with it. A disadvantage here is that the HER competes at the cathode, consuming protons and thus lowering FE.

H-type cells: These are similar to single-chamber cells but include an extra diaphragm that blocks ammonia from diffusing between cathode and anode, thus preventing ammonia oxidation. With this type of cell, HER still remains a challenge. H-type cells are used most frequently, with adjustments in reaction pressure and catalyst design often applied to address HER issues. Overall, the choice of cell configuration strongly affects the balance between NRR efficiency and suppression of competing reactions.[37]

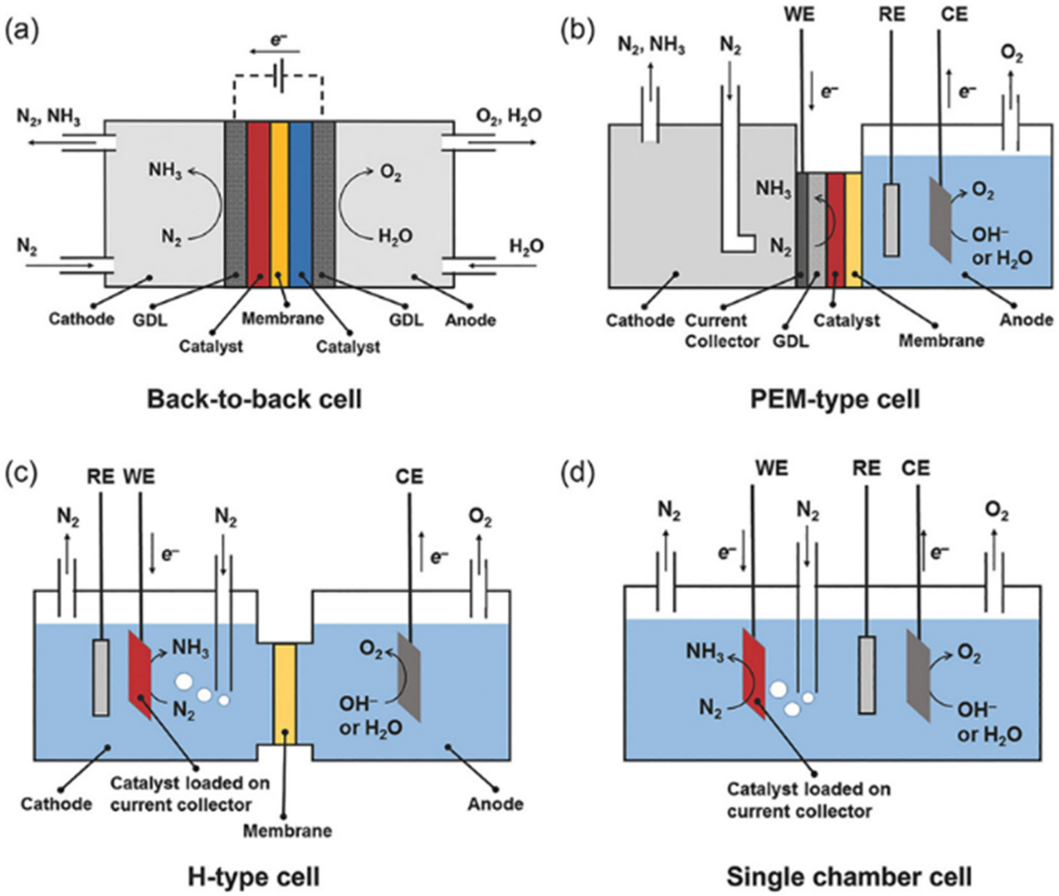


Figure 7: Types of NRR cell configurations. Taken from ref. 37 with permission from Elsevier (License. No. 6151341144666).

4.6. Challenges of NRR

Competition with the Hydrogen Evolution Reaction

The greatest obstacle to NRR (particularly in aqueous media), is the HER.[29]

$$2\ H^+ + 2\ e^- \rightleftharpoons H_2$$

HER is thermodynamically and kinetically far more favorable than NRR. It requires only two electrons, has a lower energy barrier and benefits from the high concentration of protons in aqueous environments. Consequently, most reported FE are abysmally low (<10%), that is over 90% of the input electrical energy is wasted to produce hydrogen. This makes the process economically unviable. While some reports claim FEs of 50-90%, these often occur at impractically low current densities. In addition, these reports are somewhat controversial as measurement accuracy has been questioned.[37,56]

The competition with the HER that consumes most of the available protons and electrons makes it even tougher to break the N≡N bond. Furthermore, the reaction requires the transfer of 6 protons and 6 electrons to produce two molecules of NH_3. Although hydrogenation of N_2 to NH_3 is thermodynamically feasible, the process is not spontaneous.[29]

$$N_2 + 6\,H^+ + 6\,e^- \rightarrow 2\,NH_3$$

Difficulty in activating the N≡N bond

A central challenge in NRR is the activation of the nitrogen molecules due to its strong triple bond. The N≡N bond has a dissociation energy of 941 kJ mol^{-1} and a large HOMO-LUMO gap of 10.82 eV, which makes N_2 extremely inert and resistant to reaction.[29,37]

Low yield and efficiency

Reported ammonia yields in NRR are far below industrial requirements, typically ranging between 10^{-13} and 10^{-8} mol cm^{-2} s^{-1}.[55] Even with the best-performing polymer electrolyte membrane systems, the rates (~1.13×10^{-8} mol cm^{-2} s^{-1}) remain much lower than the Department of Energy's target of 10^{-6} mol cm^{-2} s^{-1} with 90% FE.[29] In addition, N_2 solubility in aqueous electrolytes is inherently low, which restricts mass transport and limits productivity.[37]

Catalyst instability and ammonia decomposition

Elevated temperatures can enhance conductivity and catalytic activity but they also accelerate ammonia decomposition, reducing overall yield. Furthermore, catalyst surfaces often suffer from deactivation due to oxygen or water impurities. In addition, materials such as cobalt-based perovskites display volatility and reduction under low oxygen partial pressures (cathodic condition) which undermines long term operations.[56,61]

CHAPTER 5 – RENEWABLE-POWERED HABER-BOSCH PROCESS

In pursuit of net zero carbon emissions, the Renewable-Powered Haber-Bosch (RPHB) process has gained attention recently. This process offers a promising solution by substituting fossil fuel-based hydrogen with renewable hydrogen (from water electrolysis powered by renewable sources such as wind and solar energy) and by producing nitrogen through electricity-driven air separation.[67,68]

Such process not only enables sustainable fertilizer production but also enables ammonia's role as a carbon-free energy carrier. While the core concept seems straightforward, its successful implementation at a large scale is challenging both technically and economically.[69]

5.1. Integrating Renewable Feedstocks into the Haber-Bosch Process

The main modification that makes the Haber-Bosch process sustainable is the production of its core feedstocks, hydrogen and nitrogen.[67,70] The hydrogen production method of steam reforming in the traditional Haber-Bosch process is substituted with water electrolysis to promote green hydrogen production.[71] In this system, the water is split into hydrogen (H_2) and oxygen (O_2) using electricity generated from renewable sources such as solar or wind power. This method produces green hydrogen with zero direct carbon emissions at this point of production.[72–74] Electrolysis techniques using proton exchange membranes offer flexibility to variable renewables, as they can rapidly adjust hydrogen output in response to fluctuating solar or wind power. Their fast response time and low operating temperature make them ideal for intermittent energy sources. In contrast, solid oxide electrolysis cells operate efficiently under steady-state conditions because they require high and stable temperatures to maintain performance. Frequent temperature changes can cause material degradation. Therefore they are more suited for continuous operation powered by consistent electricity supplies.[72]

The nitrogen (N_2) required for the reaction is separated from the air using electricity-driven methods. Technologies such as Pressure Swing Adsorption (PSA) or cryogenic Air Separation Units (ASU) are employed for this purpose. In PSA, air is passed through adsorbent beds that selectively capture oxygen and other gases, allowing nitrogen to pass through as the main product. In contrast, ASU separates nitrogen by cryogenic distillation, where air is cooled to very low temperatures and its components are separated based on their boiling points. When these separation units are powered by renewable electricity, the nitrogen feedstock also becomes decarbonized, making both the essential inputs for ammonia synthesis energetically carbon neutral.[68,69]

5.2. Ammonia Synthesis with Renewable Inputs

Once produced, the green hydrogen from water electrolysis and nitrogen from air separation are fed into a conventional Haber-Bosch reactor, which operates at high temperatures and pressures.[73]

Figure 8 illustrates how wind energy is integrated into ammonia production. Electricity from wind turbines is used to power an electrolyzer that splits water into hydrogen and oxygen. In parallel, an ASU/ PSA extracts nitrogen from the air. The hydrogen and nitrogen streams are then fed into a Haber-Bosch reactor which produces NH_3. Storage units for H_2, N_2 and NH_3 are also part of the system, providing buffering capacity to deal with the variability of wind power. This arrangement demonstrates how renewable electricity can fully replace fossil fuels as the energy source for ammonia synthesis.[75]

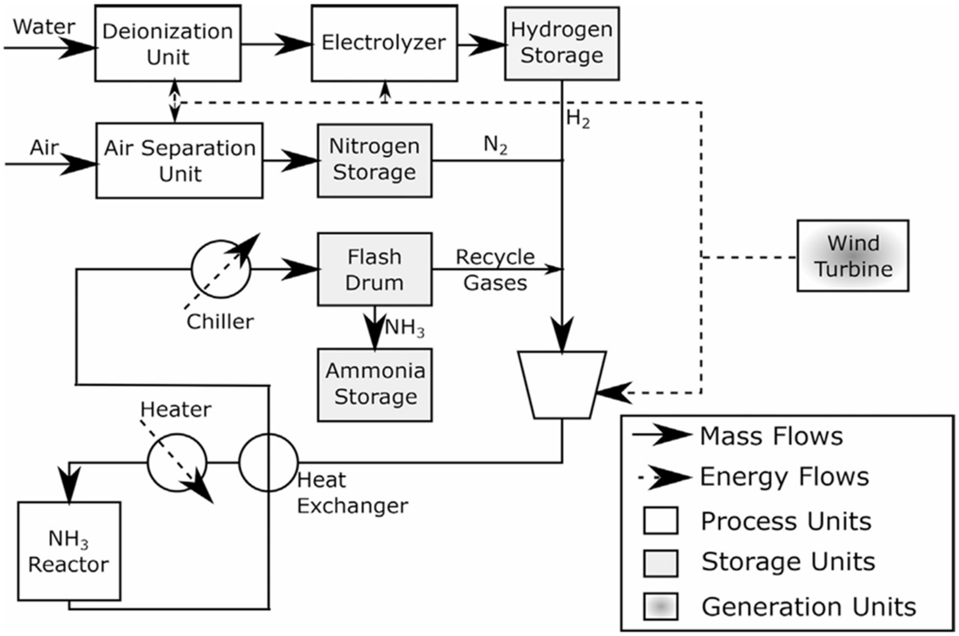


Figure 8: Flowsheet of the renewable ammonia plant built at the West Central Research and Outreach Center (WCROC), University of Minnesota. Taken from ref. 75 with permission from Elsevier (License No. 6151341412758).

5.3. Challenges of Intermittency and Reactor Inflexibility

The primary challenge with the RPHB process lies in the intermittency of the renewable power sources (solar and wind), a feature that is not compatible with the traditional Haber-Bosch process designed for steady-state operations. Conventional plants are reported to have a limited turndown ratio, that is they can only reduce output to about 60% of capacity without risking catalyst degradation or mechanical stress.[76] To address this issue, efforts are being focused on enhancing process flexibility to accommodate the intermittency of the renewable resources. Studies show that a partially flexible Haber-Bosch plant is capable of turning down to as low as 10% of its capacity by maintaining constant pressure and temperature in the synthesis loop while adjusting only the feed gas flow. This steady thermal and mechanical environment avoids catalyst sintering and equipment stress, allowing the process to adapt to intermittent renewable power without degradation. This operational flexibility allows NH_3 production to be adjusted in response to variable renewable electricity, reducing renewable energy waste and the need for large H_2 storage.[9,76] Furthermore, autothermal Haber-Bosch reactors can be adapted to accommodate variations by adjusting the hydrogen-to-nitrogen ratio and reactor pressure, which allows the plants to continue operations with a 67% reduction in hydrogen intake during low renewable source availability.[69]

5.4. Hybrid Renewable (Wind-Solar) System for Stable Operation

Relying on a single energy source is significantly more expensive than utilizing a hybrid wind-solar system. The complementary nature of wind and solar generation creates a more stable electricity supply, smoothing out variability and reducing the required capacity for generation and storage. A hybrid system can reduce the levelized cost of ammonia (average lifetime production cost per ton of ammonia) by an average of 30% compared to single source systems. Energy storage and hydrogen tanks or man-made salt caverns (artificial caves for storage) are integrated to manage intermittency.[67,76]

Figure 9 illustrates how the entire production process operates independently from the electricity grid, relying solely on renewable resources such as solar Photovoltaic (PV), wind or a hybrid of both as this can reduce variability and improve stability. The generated electricity powers the electrolyzers to produce hydrogen from water, the ASU supplies nitrogen and the Haber-Bosch synthesis loop generates ammonia. To address the variability of renewable supply, the system incorporates two types of buffering mechanisms; a battery storage with 2-8 hours capacity to smooth daily fluctuations and a hydrogen storage tank to balance seasonal variations. It also shows the integration of auxiliary components including compressors, refrigeration and oxygen management, which supports the continuous operation of the Haber-Bosch loop.[76]

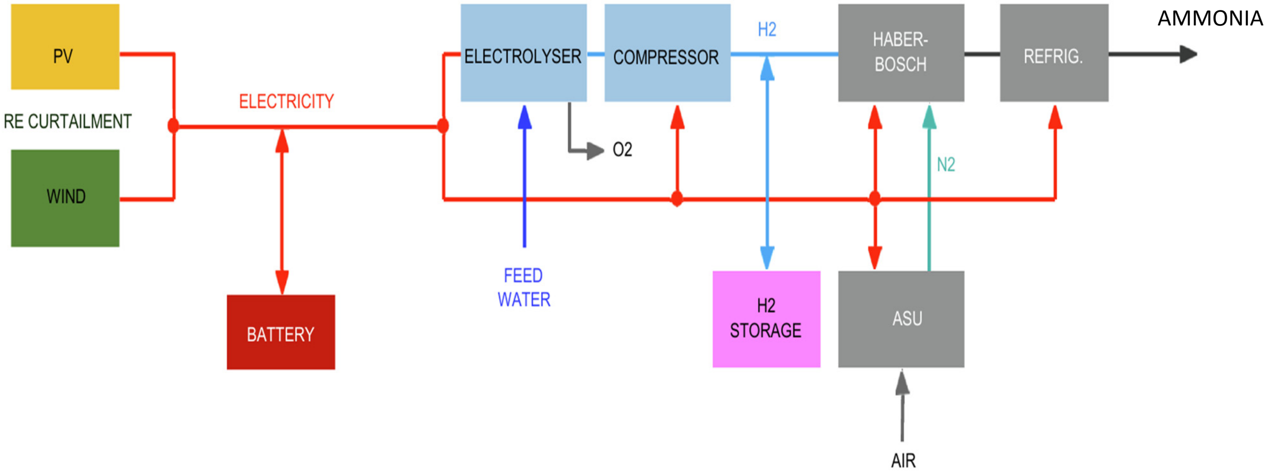


Figure 9: Schematic of the off-grid ammonia production system powered by a hybrid wind-solar system. Reproduced with permission from Wang. C.; Walsh, S.D.; Longden, T.; Palmer, G.; Lutalo, I.; Dargaville, R. *Energy Convers. Manage*. 2023, 280, 116790. Published under CC BY-NC-ND 4.0 License https://creativecommons.org/licenses/by-nc-nd/4.0/

5.5. Sustainability Benefits of the RPHB Process

There are three main benefits to using the RPHB process.

i. Replacing steam methane reforming with renewable electrolysis can reduce direct CO_2 emissions by over 75%, enabling near-zero carbon NH_3 synthesis.[38]

ii. The conversion of intermittent renewable electricity into storable NH_3 provides a dual benefit of energy storage and grid stabilization. Renewable energy integrated systems can consume surplus solar and wind power to synthesize NH_3. This load can be strategically scheduled so that it is increased during periods of oversupply and decreased during shortages. This helps to stabilize the electrical grid as well. By these means, variable renewable power can be effectively converted into a storable energy carrier.[75,77]

iii. Small-scaled decentralized RPHB plants established locally that are powered by renewable energy could reduce dependency on import and enhance fertilizer accessibility in developing regions.[68,72]

5.6. Remaining Technical and Economic Challenges

Although it is promising, the RPHB process still faces multiple technical and economic barriers. Firstly, conventional Haber-Bosch reactors are engineered for continuous operation under stable high pressure and high temperature conditions with limited operational flexibility. This is challenging with the intermittent renewable power sources previously mentioned, resulting in mechanical stress, catalyst degradation and elevated costs (associated with generation and storage infrastructure).[76]

Secondly, electrolyzers represent a major cost for the RPHB process. Although proton exchange membranes offer flexibility and solid electrolysis cells operate with higher efficiency, both suffer from significant capital costs and durability issues (i.e., short lifetime).[72] Thirdly, the overall efficiency of the energy converted to NH_3 is limited by conversion losses in both the electrolysis process and the NH_3 synthesis. The efficiency can be low as 37% or as high as 81%, depending on the system design and technology.[74,78]

Lastly, the economic viability of renewable NH_3 production is highly dependent on local conditions, including renewable resource quality, operational electricity costs at the location, and system design suitable for the location.[75]

CHAPTER 6 – SOLAR-DRIVEN AMMONIA PRODUCTION

Photocatalytic technologies are gaining attention as a sustainable approach to convert solar energy into chemical fuel.[79] Photocatalytic, solar-driven ammonia production, which aims to synthesize NH_3 directly from N_2 and water using sunlight, has emerged as a promising new pathway.[33,80] This approach is energy-saving, environmentally friendly, and can be carried out at ambient temperature and atmospheric pressure without carbon dioxide emissions. It also enables the establishment of small on-site NH_3 production units powered by renewable energy, which promotes localized synthesis near end-use locations.[23,80]

6.1. Fundamental Principles of Photocatalysis

Photocatalytic ammonia synthesis is a form of artificial photosynthesis that uses semiconductor materials to harvest/absorb solar energy in order to create electron-hole pairs capable of driving the reduction of atmospheric N_2 to NH_3. This process proceeds through two half-reactions, the reduction of nitrogen and the oxidation of water on the photocatalyst surface.[80,81]

6.1.1. The Mechanism

The mechanism of photocatalytic N_2 reduction proceeds through the following main steps:

Step 1: Photoexcitation and charge generation

When photons with energy equal or greater than the semiconductor's bandgap are absorbed, electrons are excited from the valence band (VB) to the conduction band (CB), creating electron-hole pairs.[80,81]

Step 2: Charge separation and migration

As Figure 10 illustrates, the photogenerated electrons (e^-) and the positively charged holes (h^+) then migrate to the catalyst surface where they facilitate redox reactions. Efficient separation and migration of these charge carriers are crucial to prevent recombination.[80]

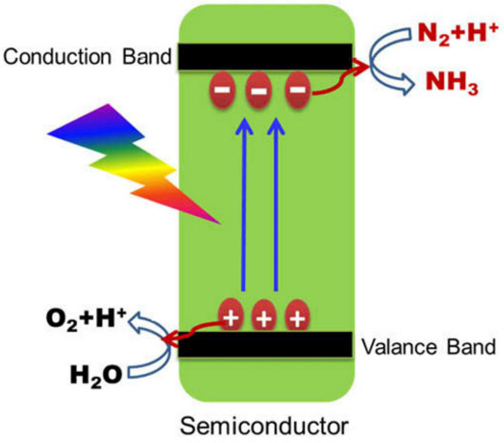


Figure 10: Overall photocatalytic N_2 reduction to NH_3 on a semiconductor-based photocatalyst. Taken from ref. 80 with permission from Elsevier (License No. 6151350587452).

Step 3: Surface redox reaction

At the surface of the semiconductor, the two half-reactions take place simultaneously.[81]

Oxidation reaction (at the valence band) : $3\ H_2O_{(l)} + 6\ h^+ \rightarrow 1.5\ O_{2(g)} + 6\ H^+_{(aq)}$

Reduction reaction (at the conduction band) : $N_{2(g)} + 6\ H^+_{(aq)} + 6\ e^- \rightarrow 2\ NH_{3(g)}$

Combining the two half-reactions gives the overall stoichiometry for photocatalytic NH_3 formation, where the electrons reduce N_2 to NH_3 while holes oxidize H_2O to O_2 and protons.[80,81]

$$N_{2(g)} + 3\ H_2O_{(l)} \rightarrow 2\ NH_{3(g)} + 1.5\ O_{2(g)} \qquad \Delta G = 7.03\ \text{eV} \approx 678\ \text{kJ mol}^{-1}$$

It is also important to point out that the photocatalytic N_2 reduction can occur via two distinct pathways. In the dissociative mechanism, the N≡N bond cleavage occurs before hydrogenation of the N atoms.[23,81] In the associative mechanism, the N≡N bond is hydrogenated stepwise prior to complete bond cleavage. The complete cleavage of the N≡N bond is avoided, significantly reducing the overall energy requirements compared to the dissociative pathway. The associative mechanism is considered to be the dominant pathway in the photocatalytic reduction of N_2 under mild conditions.[23,81]

6.1.2. Thermodynamic and Kinetic Challenges

The overall reaction of the photocatalytic formation of NH_3 is highly endothermic. The primary challenge with this method of NH_3 production lies in the activation of the strong non-polar N≡N triple bond with a dissociation energy of about 941 kJ mol^{-1}. Thus, a lot of energy is needed to cleave the triple bond of N_2, making the activation of the molecule the rate-limiting step in the process. Hence, only very limited photocatalytic activity towards NH_3 production has been achieved to date.[80,81]

6.2. Photocatalyst Materials and Design Strategies

The effectiveness of photocatalytic nitrogen fixation hinges on the semiconductor's ability to absorb light, separate charges and provide active sites for N_2 adsorption and activation.

6.2.1. Semiconductors

Metal Oxides, and in particular TiO_2, have been the most studied photocatalysts since the first demonstration of photocatalytic nitrogen fixation in 1977 by Schrauzer and Guth using a series of doped titanium oxides. However, the wide bandgap limits the material to UV light excitation. TiO_2 nanosheets, modified through doping (with Cu or C), possess oxygen vacancies and Ti^{3+} sites. These defects enhance visible light absorption and improve charge separation by acting as electron traps, thus extending the lifetime of charge carriers. This optimization has led to a significant increase in ammonia production rates.[23] Other oxides like WO_3, $BiVO_4$ and hematite (Fe_2O_3) are prominent visible-light active photocatalysts due to their approximate bandgaps of 2.6, 2.4, and 2.0 eV, respectively. This enables these materials to absorb a significant portion of the solar spectrum. However, their activity is limited due to low electrical conductivity and high rates of electron-hole recombination, which prevents the photogenerated charges from being effectively utilized in catalytic reactions.[79]

Bismuth-based catalysts such as BiOBr and Bi_5O_7Br nanotubes show enhanced charge separation and N_2 adsorption, a feature primarily attributed to the presence of oxygen vacancies that elongate the N≡N bond and lower the activation energy for N_2 reduction. Heterostructures like Bi_2MoO_6/BiOBr, when engineered with abundant oxygen vacancies, have demonstrated significantly higher ammonia yields compared to their low defect counterparts. The defects enhance light absorption and create active sites for N_2 adsorption, whereas the heterojunction interface improves charge separation. This synergy between defect engineering and interfacial charge transfer is key to the enhanced performance of these types of catalysts.[23,80]

Carbon-based catalysts such as metal-free graphitic carbon nitride (g-C_3N_4) are tunable polymers and good photocatalysts. The activity of C_3N_4 can be significantly enhanced by creating nitrogen vacancies or through heteroatom doping (e.g., with boron), which improves charge separation, reduces charge transfer resistance, and improves light absorption.[23]

Metal-organic frameworks (MOFs) offer high surface area and tunable porosity. The titanium-based MOF NH_2-MIL-125(Ti) has been engineered with amine groups and exhibits visible-light driven NH_3 production, where photoinduced ligand-to-metal charge transfer generates Ti^{3+} species that serve as active sites for nitrogen reduction, using water as the proton sources. Nonetheless, the modest NH_3 production rate (12.25 μmol g^{-1} h^{-1}) underscores the challenges of developing catalysts with practical N_2 reduction efficiency.[82] Iron-based MOFs such as MIL-101(Fe) also showed high photocatalytic activity (1007.1 μmol g^{-1} h^{-1}) due to the high electron density of the electron-rich iron centre (which lowers the activation barrier) leading to more efficient NH_3 production.[23]

6.2.2. Bio-inspired and Hybrid Systems

Biological nitrogen fixation is catalyzed by the enzyme nitrogenase under ambient temperature and pressure conditions. The FeMo-cofactor (FeMo-co) within nitrogenases is the active center which efficiently reduces one molecule of N_2 to two molecules of NH_3 using water as a proton source. This has inspired the development of biomimetic catalysts, such as FeMoS chalcogels (composed of $Mo_2Fe_6S_8(SPh)_3$ and single-cubane Fe_4S_4 clusters), that mimic the enzyme's active site cluster, enabling nitrogen activation with visible light. Another approach involves creating hybrid bio-inorganic systems (bio-hybrid systems) where synthetic inorganic photocatalysts such as CdS are used to photosensitize nitrogenase (essentially replacing ATP hydrolysis).[80,83] Furthermore, a hybrid Ag_2O-Au plasmonic-semiconductor system demonstrates high photocatalytic nitrogen reduction. Here, Au nanoparticles generate hot electrons (i.e., electrons with very high kinetic energies) through plasmonic excitation, with the Ag_2O semiconductor contributing additional photogenerated electrons. This synergistic interaction enhances charge separation and transfer, thereby improving overall catalytic activity.[40]

6.2.3. The Role of Defect Engineering

A central strategy to overcome the challenge of nitrogen activation and enhance photocatalytic nitrogen fixation is defect engineering in which the electronic structures and the chemical properties of semiconductors are altered. Various types of defects can be introduced into the catalyst design based on their atomic structure and their placement in the photocatalyst.[81]

Figure 11 shows the types of common defects in photocatalysts (and other solid-state materials). Defects can be classified based on their dimensions as point (0D) defects (vacancies, dopants), line (1D) defects (screw and edge dislocations), planar (2D) defects (grain boundaries and twin boundaries), and volume (3D) defects (void and lattice disorder). Based on their composition, defects can be further classified as oxygen- (OV), nitrogen- (NV), sulfur- (SV), carbon- (CV) or fluorine-vacant (FV).[81]

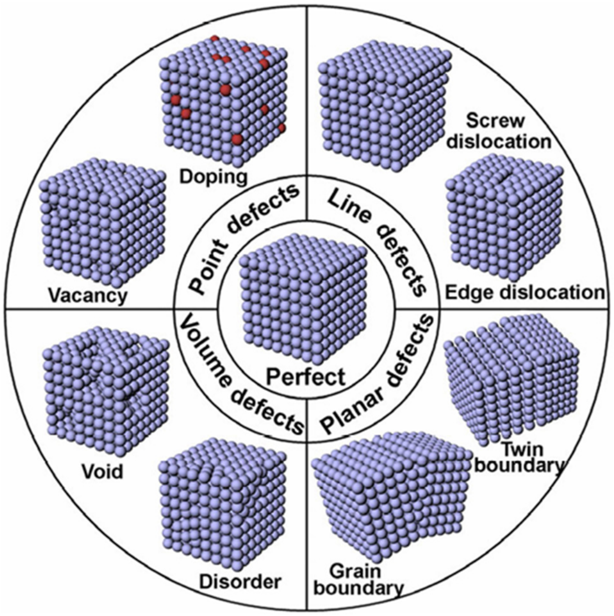


Figure 11: Types of common defects in semiconductor photocatalysts. Reproduced with permission from Shen, H.; Yang, M.; Hao, L.; Strunk, J.; Sun, Z. *Nano Res.* 2022, 15, 2773-2809. Published under a CC BY 4.0 License https://creativecommons.org/licenses/by/4.0/

Surface defects can enhance the adsorption and activation of a reacting molecule, whereas excessive bulk defects act as recombination centers for photogenerated charges, thereby reducing the photocatalytic efficiency. Defect engineering strategies are generally divided into post-treatment methods, which include chemical or thermal reduction, force-induced techniques such as plasma, alkali etching, ultrasonic processing and in-situ approaches (where oxygen vacancies are generated by light during photoreduction). By introducing and controlling specific defects, the semiconductors can achieve a broadening of the light absorption range and an enhancement of charge carrier separation and migration. However, achieving an optimal defect concentration remains challenging.[81]

Oxygen vacancies in TiO_2, BiOBr, Bi_5O_7Br nanotubes and WO_3, and sulfur vacancies in MoS_2/CdS composites provide localized electrons that act as active sites, significantly improving N_2 adsorption and activation under mild conditions. These vacancies function analogously to catalytic sites in natural enzymes by facilitating charge transfer and lowering activation barriers.[23,80]

6.3. Challenges and Efficiency Limitations

Despite promising advances, photocatalytic solar-driven ammonia synthesis faces critical challenges that hinder its practical applications.

The solar to chemical conversion efficiency currently remains very low (typically below 0.1%) and ammonia yields are in the nmol to µmol per hour per gram of catalyst range, which is far below industrial requirements.[1,80] In addition, photo-corrosion and loss of active defects in many semiconductor materials lead to catalyst deactivation after a few reaction cycles. Moreover, rapid recombination of photogenerated electrons and holes reduces quantum efficiency.[23,79] Furthermore, the HER is a major competitor for photogenerated electrons and is a thermodynamically favorable side reaction, which significantly reduces NH_3 production. Readily available protons can be reduced to H_2, a reaction that often outcompetes the more complex multi-step N_2 reduction.[23,40]

However, certain strategies can be used to favor NH_3 formation over HER by altering the catalytic environment. For instance, employing ionic liquids with lower water content can increase N_2 solubility while simultaneously suppressing proton reduction side reactions. Likewise, introducing a hydrophobic environment around the catalyst can regulate proton accessibility and enrich the N_2 concentration, thereby favoring selective N_2 adsorption and activation.[40,83]

CHAPTER 7 – BIOLOGICAL NITROGEN FIXATION

Given the urgency to mitigate environmental pollution associated with the Haber-Bosch process, Biological Nitrogen Fixation (BNF) has emerged as a naturally evolved and sustainable alternative. BNF is a fundamental biochemical process that sustains life on Earth by converting inert atmospheric N_2 into NH_3.[8] This reduction of N_2 is carried out by the enzyme complex nitrogenase present in certain prokaryotic microorganism (diazotrophs) under ambient conditions, and is powered by cellular energy rather than the fossil fuels used in the industrial method. This chemical transformation accounts for the majority of reactive nitrogen entering the biosphere.[8,84]

In agriculture, nitrogen fixation is critical with about 90 million tons of NH_3 supplied annually through BNF. This makes BNF a major natural contributor of new nitrogen to agriculture and hence, food supply.[85]

Symbiotic BNF in leguminous crops can contribute between 200-300 kg N ha^{-1} yr^{-1}, which accounts for about 21% of global biologically fixed nitrogen. This can substantially reduce fertilizer dependency and sustain soil fertility.[8] The increasing demand for sustainable nitrogen fixation has ignited interest in understanding and optimizing the capacity of BNF beyond its natural limitations. Most staple crops (wheat and maize) do not fix nitrogen. Recent developments in synthetic biology and metabolic engineering now enables nitrogenase activity in non-diazotrophs such as *Escherichia coli*, *Saccharomyces cerevisiae*, *Synechococcus elongatus* as well as algae and other plants (barley, wheat, maize).[86,87]

7.1. Mechanism of BNF

The nitrogenase enzyme complex is the metalloenzyme system that is capable of breaking the N≡N triple bond and catalyzes the stepwise reduction of N_2 to NH_3 at atmospheric pressure and room temperature.[88] The nitrogenase complex is comprised of two metalloproteins: the dinitrogenase reductase (Fe-protein) and dinitrogenase. The latter enzyme exists as three metal variants based on its active site; Molybdenum- (MoFe-protein), Vanadium- (VFe-protein) and Iron-only (FeFe-protein) nitrogenase. The most widespread and well-characterized form of the enzyme is the molybdenum-dependent nitrogenase (Mo-nitrogenase) which serves as the archetype for all nitrogen-fixing systems.[8]

The Fe-protein is an α_2 homodimer containing a [4Fe-4S] cluster, which hydrolyses ATP and donates electrons sequentially to the MoFe-protein. The MoFe-protein is an $\alpha_2\beta_2$ heterotetramer consisting two metal co-factors, the P-cluster ([8Fe-7S]) and the FeMo-cofactor ([Mo-7Fe-9S-C-homocitrate]), which constitutes the active catalytic center.[89]

Nitrogenase operates via a deficit-spending mechanism; the electrons are transferred from the Fe-protein to the P-cluster and then to the FeMo-cofactor, where N_2 binding and stepwise proton-coupled reduction occurs with the elimination of H_2, achieving an Faradaic Efficiency (FE) of 75%.[84]

The overall reaction that occurs in the nitrogenase complex can be expressed as follows:

$$N_2 + 8\ H^+ + 8\ e^- + 16\ ATP \rightarrow 2\ NH_3 + H_2 + 16\ ADP + 16\ P_i$$

The stoichiometry reveals that the enzyme requires (at least) 16 ATP molecules per a molecule of N_2 reduced and that the reaction is obligatorily coupled with H_2 evolution, which consumes reducing power without contributing to NH_3 yield.[89]

The main constraint of nitrogenase is its extreme sensitivity to oxygen, which irreversibly damages its Fe-S clusters. Diazotrophs therefore employ protection mechanisms; including high respiratory rates to maintain low intracellular O_2 (e.g., *Azotobacter* species), spatial segregation of fixation in heterocyst (e.g., cyanobacteria) or temporal separation from photosynthesis, to maintain low internal oxygen levels.[8,90]

Genetically, proteins involved in nitrogen fixation are encoded by the *nif* (nitrogen fixation) gene cluster, which includes structural genes (*nif*H, *nif*D, *nif*K) for the catalytic subunits and accessory genes (*nif*B, *nif*E, *nif*N, *nif*V, *nif*S, *nif*M) for cofactor assembly.[87] Expression is tightly regulated by *nif*A and *nif*L in response to oxygen and ammonium concentrations.[90]

Figure 12 illustrates the core *nif* gene cluster and its biochemical interactions during molybdenum-iron nitrogenase maturation and catalysis. The structural genes *nif*H, *nif*D and *nif*K encode the nitrogenase catalytic subunit responsible for electron transfer and N_2 reduction, while accessory genes such as *nif*B, *nif*E, *nif*N, *nif*V, *nif*S, and *nif*M participate in Fe-S cluster and FeMo-cofactor assembly. The *nif*B gene encodes NifB, which catalyses the formation of the NifB-co precursor from [4Fe-4S] clusters. The accessory genes *nif*E and *nif*N encode NifEN, a maturation complex that converts NifB-co into the FeMo-cofactor. This FeMo-cofactor is then incorporated into the catalytic NifDK protein, encoded by *nif*D and *nif*K, forming the active site where N_2 is reduced to NH_3. Electrons are transferred from the NifH protein (Fe-protein) encoded by *nif*H gene, through ATP hydrolysis to drive the electron transfer to the MoFe-protein.[87]

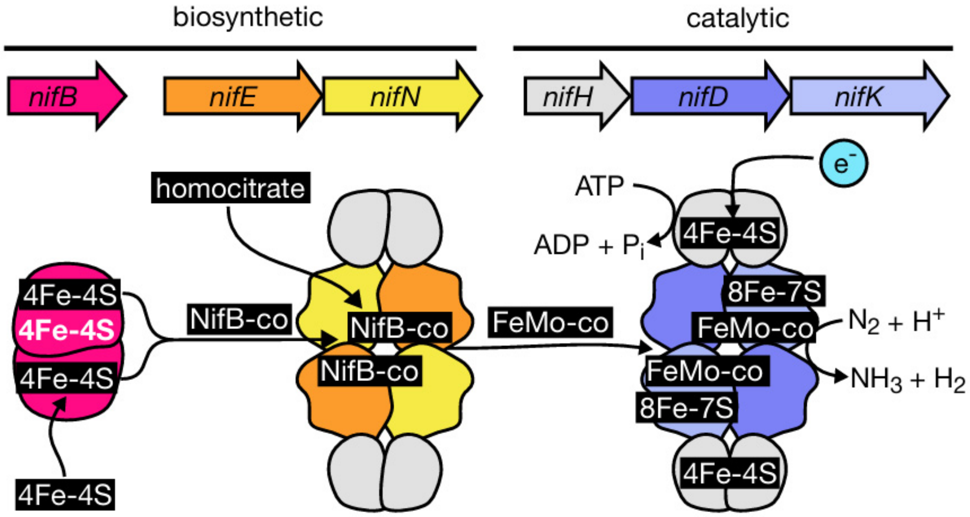


Figure 12: Organization and function of the *nif* gene cluster for biological nitrogen fixation. Reproduced with permission from Bennett, E. M.; Murray, J. W.; Isalan, M. *BioDesign Res.* 2023, 5, 0005. Published under a CC BY 4.0 License https://creativecommons.org/licenses/by/4.0/

7.2. Engineered Microbial Systems for Ammonia Production

7.2.1. Bacterial Gene Cluster Engineering

Bacteria represent the most extensively studied organisms for biological ammonia synthesis. The enzyme nitrogenase has been successfully expressed heterologously in *Escherichia coli*, through the transfer of the *nif* gene cluster from *Klebsiella oxytoca*, a landmark in synthetic nitrogen fixation. The cluster encodes the full set of structural, assembly and regulatory genes required for nitrogenase function.[86,91]

As mentioned previously, the nitrogenase complex is encoded by a cluster of *nif* genes, which include those encoding the catalytic subunits as well as the accessory genes required for Fe-S cluster assembly and electron transfer. By introducing a minimal set of nine *nif* genes from

Paenibacillus into *E. coli*, Li and colleagues achieved partial nitrogenase activity (~10% of natural fixation). This activity was subsequently increased to ~50% through co-expression of Fe-S cluster assembly genes from *Klebsiella oxytoca* and electron transport genes from *Paenibacillus.*[94]

Figure 13 illustrates the genetic streamlining of N_2 fixation in *Paenibacillus* compared with the multi-operon system of *Klebsiella oxytoca*. This comparison demonstrates that nitrogenase function can be sustained by a minimal nine-gene cluster despite lacking several auxiliary components present in Gram-negative diazotrophs.[92]

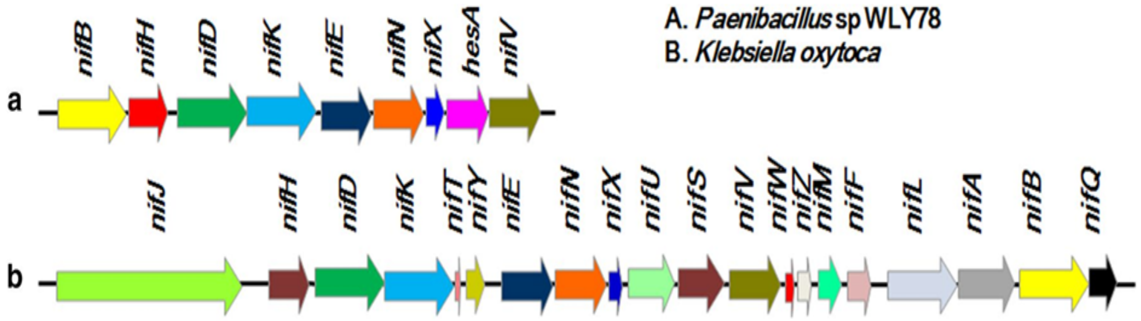


Figure 13: Comparison of *nif* gene clusters of *Paenibacillus* vs *Klebsiella oxytoca*. Reproduced with permission from Li, X.-X.; Liu, Q.; Liu, X.-M.; Shi, H.-W.; Chen, S.-F. Using Synthetic Biology to Increase Nitrogenase Activity. *Microb*. *Cell Factories* 2016, 15 (1), 43. Published under a CC BY 4.0 License https://creativecommons.org/licenses/by/4.0/

Restructuring native *nif* clusters into synthetic systems can often disrupt the coordinated expression required for nitrogenase activity. Another innovation in the field of cluster engineering involved a fusion of multiple *nif* genes into operons (cluster of genes transcribed together) to ensure correct stoichiometry and coordinated expression of nitrogenase components. This approach helped to re-balance the uneven subunit expression, thereby enabling correct enzyme assembly and improving the strain's ability to fix atmospheric nitrogen.[87,92]

7.2.2. Protective Adaptations Against Dioxygen

Natural strategies for protecting nitrogenase from oxygen are also being explored to enhance activity in engineered systems. For instance, *Pseudomonas stutzeri* forms cyst-like structures encased in extracellular polymeric substances that create localized microaerobic zones, whereas *Azotobacter vinelandii* secretes extracellular alginate, which physically blocks oxygen and shields its nitrogenase.[93,94]

7.2.3. Yeast Systems and Cell-surface Biocatalysis

Yeast (*Saccharomyces cerevisiae*) is a eukaryotic host with advanced protein-folding and assembly capacities, making it a promising platform for expressing complex nitrogenase enzymes. Nitrogenase expression in yeast mitochondria has been achieved at partial level but remains limited by challenges in protein solubility, stability and assembly.[95,96] The use of thermostable nitrogenase variants from heat-tolerant organisms such as *Hydrogenobacter thermophilus* has improved performance, suggesting that such enzymes may be better suited at higher mitochondrial temperature.[97]

Beyond nitrogenase expression, yeast has also been engineered for extracellular NH_3 production using a cell-surface enzyme display system. In this system, catalytic enzymes are immobilized on the yeast cell wall, where they convert external nitrogen-containing substrates such as glutamine into NH_3. The released NH_3 accumulates outside the cell, avoiding re-assimilation and simplifying product recovery.[98] Using this approach, engineered yeast displaying *E. coli* glutaminase on its surface produced 3.34 $g\ L^{-1}$ of NH_3 from 32.6 $g\ L^{-1}$ glutamine with 83% conversion.[101] To demonstrate its practicability, the same engineered yeast was employed to produce NH_3 from

Okara, a soybean residue, that is a protein- and glutamine-rich by-product of tofu and soymilk production, typically discarded as food waste. After mild enzymatic pretreatment of Okara to release amino acids, the yeast converted the liberated glutamine into NH_3, illustrating a sustainable route for converting food waste to bio-ammonia.[86,99]

7.2.4. Bioelectrocatalytic Approaches and Synthetic Symbiosis

Recent advances in nitrogenase bioelectrocatalysis couple enzymatic catalysis with electrochemical energy, enabling NH_3 synthesis under ambient conditions. Electrochemical systems employing artificial redox mediators such as methyl viologen replacing biological electron donors, can shuttle electrons from the electrodes to nitrogenase, achieving N_2 reduction with FE up to 58.8% with an NH_3 yield of 2.1 μmol mg^{-1} h^{-1}.[100] Moreover, direct electron delivery to the catalytic MoFe-protein bypassing ATP hydrolysis and the Fe-protein has been realized using photoexcited (by solar energy) CdS nanorods or polymer-modified electrodes which produced ammonia at 75 turnovers min^{-1}.[101] These simplified single enzyme systems demonstrate that nitrogenase activity can be sustained by electrical or solar inputs, marking a key step towards renewable and low energy NH_3 production.[84]

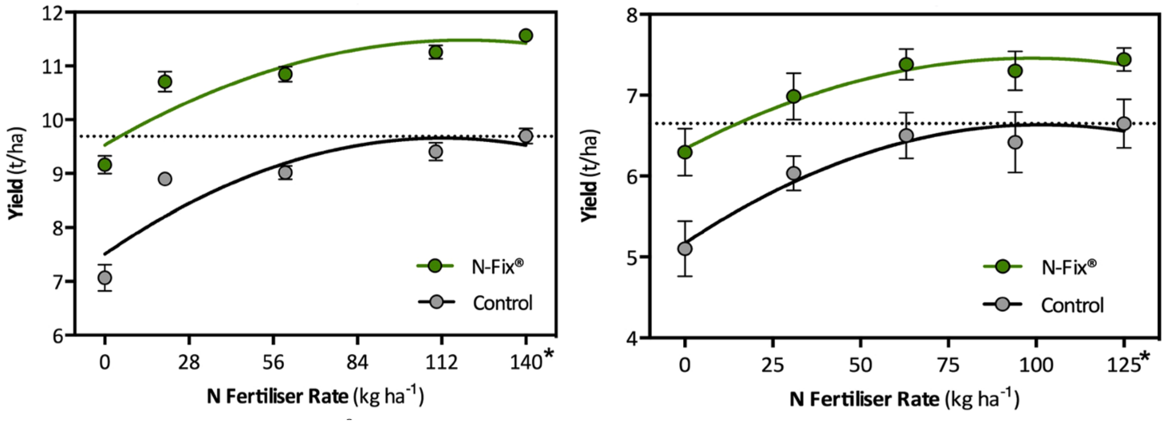
Efforts on engineering symbiotic relationships synthetically focus on establishing interactions between nitrogen-fixing bacteria and cereal crops. This creates systems where plants produce orthogonal molecules like rhizopene to regulate *nif* gene expression in associated bacteria. Establishing such synthetic symbiosis requires nutrient exchange to support bacterial growth and to offset the metabolic cost of nitrogen fixation. Yet, survival of this engineered symbiosis in a real environment remains a challenge.[87]

7.2.5. Agricultural Integration: Endophytic Diazotrophs and Crop Productivity

Expanding BNF beyond legumes into cereals has been a century-long challenge. A major breakthrough came with the discovery of *Gluconacetobacter diazotrophicus* (Gd), which is an aerobic and endophytic bacterium, capable of intracellular colonization of non-legume crops such as maize, rice, wheat and tomato.[102]

Gd safeguards its nitrogenase through exopolysaccharide synthesis, creating a localized barrier that restricts oxygen diffusion and permits fixation under ambient O_2 levels. The absence of nitrate reductase renders nitrogenase only partially sensitive to ammonium, thus displaying activity even in the presence of chemical fertilizers. For example, field trials with NFix® (a seed inoculant biofertilizer containing Gd) have shown yield gains of roughly 1 t ha^{-1} in maize and wheat under full fertilizer application.[102]

Figure 14(A) shows maize yields from field trials in Germany, comparing NFix®-inoculated seeds with uninoculated controls under five nitrogen fertilizer levels. Across fertilizer rates, inoculated plants consistently produced higher yields, with the NFix® treatment reaching or exceeding the full recommended fertilizer rate, which is normally applied for maximum yield (shown as a dotted line). Figure 14(B) shows parallel results for wheat trials in the UK, where NFix®-treated seeds similarly out-performed controls at every nitrogen level. Together, these results demonstrate that Gd maintains high productivity even in the presence of full nitrogen inputs, confirming its compatibility with conventional fertilization and its potential for reducing fertilizer dependence. In addition, Gd has been shown to enhance photosynthetic performances and water-use efficiency in host plants, indicating metabolic benefits beyond nitrogen fixation.[102]



(A) **(B)**

Figure 14: Yield performances of (A) maize and (B) wheat inoculated with NFix® compared to uninoculated controls under varying nitrogen fertilizer rates. Reproduced with permission from Dent, D.; Cocking, E. Establishing Symbiotic Nitrogen Fixation in Cereals and Other Non-Legume Crops: The Greener Nitrogen Revolution. *Agric. Food Secur.* 2017, 6 (1), 7. Published under a CC BY 4.0 License https://creativecommons.org/licenses/by/4.0/

7.3. Critical Challenges

Despite remarkable progress, several barriers still prevent BNF from becoming a successful replacement for the Haber-Bosch process. For instance, nitrogenase turnover frequencies (1-5 s^{-1}) are orders of magnitude lower than those of industrial catalysts (10^4-10^5 s^{-1}). The requirement of 16 ATP per N_2 molecule represents a heavy energy demand. Bioelectrocatalytic systems offer an external energy source, but currently exhibit low catalytic turnover frequencies (0.1-75 min^{-1}).[84] However, energy analyses show that the Haber-Bosch process consumes 8-15 kWh kg^{-1} NH_3, whereas photosynthetically driven BNF uses only 1-2% of equivalent solar energy. Furthermore, replacing 20% of industrial ammonia with biological equivalents could reduce global CO_2 emissions by 300-400 million tons annually.[84,102]

Oxygen sensitivity is another challenge in this alternative method. The Fe-S clusters of nitrogenase are destroyed by oxygen, restricting activity to anaerobic or microaerobic conditions.[84,90] Although natural protection mechanisms such as heterocyst formation and exopolysaccharide barriers exist, they are species-specific and energy-intensive.[102]

Finally, the genetic and regulatory complexity of the nitrogenase system represents a major hurdle. Functional nitrogenase expression requires more than 17 *nif* genes, along with tight regulation via *nif*A/*nif*L to balance production of nitrogenase subunits as well as accessory proteins and for compatible cofactor assembly. Transferring such operons into eukaryotic cells demands conversion of bacterial polycistrons into individually regulated units compatible with eukaryotic transcription, which is a major challenge in synthetic biology.[90,103]

CHAPTER 8 - CONCLUSION

Ammonia is one of the most vital chemical substances in modern civilization with its wide applications in agriculture, industry, and recently, with the transition to clean energy. However, the conventional industrial production of ammonia by the Haber-Bosch process (which was an industrial milestone of the twentieth century) has now become a burden for the environment. Its immense fossil fuel dependency, high energy consumption and large carbon footprint have made it a central focus for decarbonization in the chemical industry. As the world now moves towards net-zero emissions, the challenge is not only to supply ammonia but to produce it through sustainable production pathways which are carbon-neutral.

Efforts toward sustainable ammonia production have therefore focused on integrating renewable energy sources, and designing advanced catalytic systems capable of operating under mild conditions. This has led to the introduction of diverse alternative pathways, including Electrocatalytic Nitrate Reduction (ENR), the electrochemical Nitrogen Reduction Reaction (NRR), the Renewable-Powered Haber-Bosch process, Photocatalytic Ammonia Production, and Biological Nitrogen Fixation (BNF).

Each of these pathways represents a distinct approach ranging from electrochemical and photochemical to biological and hybrid engineering, which reflects the diversification of sustainable ammonia synthesis research. These aforementioned routes differ not only in their energy sources and environmental impact (which are of main concern for moving towards sustainable ammonia production), but also in their operational environment, technological maturity, and scalability. A comparative assessment of these methods is therefore essential to appreciate their respective potentials and limitations in shaping a future nitrogen economy.

Table 4 summarizes the operating conditions, energy requirements and carbon footprint for the conventional Haber-Bosch process and the emerging pathways.

Table 4: Comparison of energy consumption and associated CO_2 emissions by ammonia synthesis pathways

Pathway	Energy consumption	CO_2 emissions
Conventional Haber-Bosch Process	400-500 °C, 150-300 atm	High
Electrocatalytic Nitrate Reduction (ENR)	Room temperature, 1 atm	Zero
Electrochemical Nitrogen Reduction Reaction (NRR)	Room temperature, 1 atm	Zero
Renewable-powered Haber-Bosch process (RPHB)	400-500 °C, 150-300 atm	Low
Solar Ammonia Production	Solar energy, room temperature	Zero
Biological Nitrogen Fixation (BNF)	Ambient condition	Zero

While the Haber-Bosch process continues to rely on high temperature, high pressure and has high CO_2 emissions, the alternative methods operate under considerably milder conditions and offer low to zero-emission when supported by renewable energy. This highlights that the emerging technologies have the potential to reduce the energy intensity and the environmental impact caused by CO_2 emissions.

Table 5 provides a comparative assessment of the conventional Haber-Bosch process with emerging sustainable ammonia synthesis pathways in terms of their operating principles, technological framework and key advantages.

Table 5: Comparison of core principle, advantages and limitations of conventional and emerging ammonia production pathways

Pathway	Core Principle	Key advantages	Major challenges
Conventional Haber-Bosch Process	Catalytic synthesis of NH_3 from N_2 and H_2 at high temperature and pressure using fossil-based hydrogen	Technologically mature and globally established High production efficiency and reliability Well integrated industrial infrastructure	Extremely energy- and carbon-intensive Relies on fossil fuels for H_2 production Inflexible for renewable integration
Electrocatalytic Nitrate Reduction (ENR)	Electrochemical reduction of NO_3^- to NH_3 using renewable electricity under ambient conditions	Dual environmental benefit of producing ammonia and reduce nitrate pollution Operates under mild conditions High selectivity possible with optimized catalysts	Requires nitrate feedstock (which is not universally available) Catalyst degradation and mass transport limitation Competing Hydrogen Evolution Reaction (HER)

Table 5 (continued)

Electrochemical Nitrogen Reduction Reaction (NRR)	Direct reduction of atmospheric N_2 and H_2O using renewable electricity	Completely carbon-free when powered by renewables Operates at ambient temperature and pressure Potential for decentralized and modular production	Low NH_3 yield and Faradaic Efficiency (FE) Competition from HER Difficulty in reproducibility and contamination issues
Renewable-powered Haber-Bosch process (RPHB)	Conventional Haber-Bosch process powered by green hydrogen (from electrolysis) and renewable electricity	Technologically proven and scalable Can fully eliminate fossil fuel dependency Compatible with existing infrastructure	High capital and operating cost Process inflexibility with intermittent renewables Hydrogen storage and supply issues
Solar Ammonia Production	Solar-driven reduction of N_2 and H_2O on semiconductor photocatalysts under ambient conditions	Utilizes abundant solar energy Operates under mild, carbon-free conditions Potential for off-grid, decentralized production	Extremely low solar-to-ammonia conversion (< 0.1%) Catalyst instability and recombination losses

Table 5 (continued)

Biological Nitrogen Fixation (BNF)	Enzymatic reduction of N_2 to NH_3 by nitrogenase in diazotrophic microorganisms or engineered systems	Operates at ambient conditions with no CO_2 emissions Enhances soil fertility naturally Integrates directly into agriculture	Low catalytic rate and oxygen sensitivity Complex gene regulation and energy (ATP) requirements Field performance variability

While the Haber-Bosch process remains the industrial benchmark due to its high productivity and technical maturity, the alternatives demonstrate innovative approaches to lower energy and environmental impact. Table 5 also highlights the persisting challenges in each pathway which might prevent them from achieving full industrial viability. Overall, the comparison underscores that while no single approach fully meets the simultaneous goal of efficiency and environmental integrity, each contributes valuable insight towards the long-term sustainable NH_3 production goal.

Table 6 compares the sustainability potential and practical feasibility of both conventional and emerging ammonia production pathways. The comparison shows a clear trade-off between technical maturity and environmental impact.

Table 6: Comparative assessment of conventional and emerging ammonia production pathways based on their relative sustainability potential and practical feasibility

Pathway	Sustainability	Practicality
Conventional Haber-Bosch Process	Low sustainability (High CO_2 emissions and fossil fuel dependence)	Very high (Industrially dominant and fully commercialized worldwide)
Electrocatalytic Nitrate Reduction (ENR)	High environmental sustainability (Pollution removal and renewable-powered)	Moderate (Feasible at lab scale but industrial scalability limited by nitrate availability)
Electrochemical Nitrogen Reduction Reaction (NRR)	High theoretical sustainability, but current FE is too low	Low to moderate (Still largely at the research stage)
Renewable-powered Haber-Bosch process (RPHB)	Very high sustainability (Solar-driven, zero emissions)	Low (Early stages of research, requires major breakthroughs)
Solar Ammonia Production	Excellent sustainability (Biological, renewable energy driven)	Moderate (Scalable in agriculture but not for industrial NH_3 demand)
Biological Nitrogen Fixation (BNF)	High sustainability (Zero-carbon hydrogen feed)	High (Feasible for agricultural applications)

While the conventional Haber-Bosch remains the most practical and industrially established, it is also the least sustainable due to its fossil fuel dependence. In contrast, solar ammonia and BNF achieve excellent sustainability through ambient and carbon-free operation, but they are constrained by low efficiency and limited scalability. On the other hand, the renewable-powered Haber-Bosch and electrochemical/electrocatalytic approaches occupy a middle ground, offering near-term decarbonization with partial industrial compatibility. Overall, the table highlights that the progress towards sustainable NH_3 production will likely rely on combining the practicality of established systems with the environmental sustainability of green technologies. Therefore, from a critical perspective, the renewable-powered Haber-Bosch and electrochemical/electrocatalytic approaches appear to be the most promising short-term strategies for industrial decarbonization with immediate implementation. In contrast, the solar ammonia and BNF processes represent long-term transformative solutions, which require further research to achieve industrial relevance.

In conclusion, a single replacement for the Haber-Bosch process is very unlikely with the current level of development of each emerging alternative. Instead, progress will depend on hybrid systems that can balance practicality with environmental sustainability. In short, the integration of these diverse methodologies will determine the pace at which global ammonia production can transition towards carbon neutrality, underscoring the urgent need for coordinated innovation, investments, and policy support to achieve a sustainable nitrogen economy.

CHAPTER 9 – FUTURE DIRECTIONS AND PERSPECTIVES

Although the transition towards sustainable ammonia is progressing, the emerging pathways yet face significant scientific and practical challenges, which limits their real-world applications. Since no single pathway by itself is capable of replacing the Haber-Bosch process at a global scale, future research must therefore focus on overcoming the fundamental limitations of each method.

Electrochemical Nitrogen Reduction (NRR) is a promising pathway in terms of decentralized ammonia production but its applicability is often limited by low selectivity and the dominance of the competing HER. Moreover, much of the field remains overly focused on catalyst design while overlooking system engineering factors such as mass transport and long-term operational stability. As a result, scaling the process beyond laboratory conditions remains challenging. Therefore, future research should focus more on strategies that effectively suppress HER to allow more selectivity for N_2 activation as well as to develop catalysts that can maintain activity and stability over extended periods of operation. The reaction environment should limit the unwanted proton availability. It is also equally important to establish standardized testing protocols (to aid the comparison between studies) and well-designed reactor systems that can enhance mass transport and provide reliable performance.

Electrochemical Nitrate Reduction (ENR) stands out for its high efficiency and dual benefit of pollutant removal but its long-term scalability is constrained by the inconsistent and limited nitrate feedstock which is insufficient to support large-scale ammonia production. The challenge therefore lies not in the reactivity but in applicability. Most published experiments heavily rely on simplified laboratory electrolytes that do not reflect real wastewater conditions and might overestimate catalytic performances as real wastewater contains variable nitrate concentrations and impurities (chloride, organic matter, metal ions) that can poison catalysts or sometimes can alter reaction pathways. Moreover, nitrate availability is in itself a variable and could be regionally limited. Ultimately, ENR realistically cannot meet global ammonia demand with the current state of development. Future research should focus on evaluating catalysts using realistic nitrate sources/wastewater, improving tolerance to impurities and developing reactor configurations that can adapt to variable nitrate concentrations. Such insight is essential to decide whether ENR can transition from wastewater treatment to practical ammonia production.

The Renewable-Powered Haber-Bosch (RPHB) process is currently the closest to commercial deployment with the highest degree of technical maturity compared to other alternatives as it relies on an already established industrial process. Since the intermittent nature of renewable energy conflicts with the steady-state operation required by the Haber-Bosch reactors, making the reactor design more flexible is a critical need. Even partial load fluctuations can disrupt temperature and pressure balance, affecting catalyst life and mechanical stability. Moreover, producing H_2 through electrolysis is more expensive than conventional methods. In addition, the system requires additional energy storage to manage the fluctuations in renewable power. These issues further increase the capital as well as operational costs of the process. Therefore, future research should prioritize improving reactor durability, reducing H_2 production cost, and developing systems which can function efficiently under variable energy input.

Solar ammonia production fits well with the idea of green ammonia production. However, the solar-to-ammonia conversion efficiencies are below practical levels because of issues with photon adsorption and charge separation. In addition, the catalytic stability is poor due to rapid photocorrosion and structural degradation limiting catalyst lifetime. To address these shortcomings, future research will require the development of photocatalysts capable of maintaining structural and chemical stability under continuous solar exposure. Furthermore, materials need to be engineered to facilitate more efficient charge separation and transfer. Progress in these areas should be accompanied by the design of photochemical systems that operate effectively under real sunlight conditions using only water as the electron and proton source.

Biological Nitrogen Fixation (BNF) is the most sustainable and valuable pathway for reducing fertilizer dependence. Yet, it is restricted by biochemical constraints. Nitrogenase is highly oxygen-sensitive and requires lots of energy, making it difficult to achieve high ammonia yields outside of tightly controlled settings. Furthermore, engineered microbial systems often perform well in controlled environments but show inconsistent results under real field conditions. Developing nitrogenase variants or microbial hosts that can tolerate oxygen and developing systems that can help these organisms survive and function in real soil environments, is therefore paramount.

Overall, sustainable ammonia production could be achieved in the future with the parallel advancement of multiple pathways. Progress must extend beyond catalyst testing and discovery to include advanced reactor engineering, performance evaluation under realistic conditions, and integration of renewable energy. Only through this coordinated approach, these emerging technologies can evolve into a reliable, scalable and economically as well as environmentally viable contributor to a low-carbon ammonia industry.

REFERENCES

(1) Ghavam, S.; Vahdati, M.; Wilson, I. A. G.; Styring, P. Sustainable Ammonia Production Processes. *Front. Energy Res.* **2021**, *9*, 580808. https://doi.org/10.3389/fenrg.2021.580808.

(2) Adeniyi, A.; Bello, I.; Mukaila, T.; Sarker, N. C.; Hammed, A. Trends in Biological Ammonia Production. *BioTech* **2023**, *12* (2), 41. https://doi.org/10.3390/biotech12020041.

(3) Brightling, J. Ammonia and the Fertiliser Industry: The Development of Ammonia at Billingham, A History of Technological Innovation from the Early 20th Century to the Present Day. *Johnson Matthey Technol. Rev.* **2018**, *62* (1), 32–47. https://doi.org/10.1595/205651318X696341.

(4) Pfromm, P. H. Towards Sustainable Agriculture: Fossil-Free Ammonia. *J. Renew. Sustain. Energy* **2017**, *9* (3), 034702. https://doi.org/10.1063/1.4985090.

(5) Cai, S.; Zhao, X.; Yan, X. Towards Precise Nitrogen Fertilizer Management for Sustainable Agriculture. *Earth Crit. Zone* **2025**, *2*, 100026. https://doi.org/10.1016/j.ecz.2025.100026.

(6) Tallaksen, J.; Bauer, F.; Hulteberg, C.; Reese, M.; Ahlgren, S. Nitrogen Fertilizers Manufactured Using Wind Power: Greenhouse Gas and Energy Balance of Community-Scale Ammonia Production. *J. Clean. Prod.* **2015**, *107*, 626–635. https://doi.org/10.1016/j.jclepro.2015.05.130.

(7) Zamfirescu, C.; Dincer, I. Using Ammonia as a Sustainable Fuel. *J. Power Sources* **2008**, *185* (1), 459–465. https://doi.org/10.1016/j.jpowsour.2008.02.097.

(8) Soumare, A.; Diedhiou, A. G.; Thuita, M.; Hafidi, M.; Ouhdouch, Y.; Gopalakrishnan, S.; Kouisni, L. Exploiting Biological Nitrogen Fixation: A Route Towards a Sustainable Agriculture. *Plants* **2020**, *9* (8), 1011. https://doi.org/10.3390/plants9081011.

(9) Rouwenhorst, K. H. R.; Krzywda, P. M.; Benes, N. E.; Mul, G.; Lefferts, L. Ammonia Production Technologies. In *Techno-Economic Challenges of Green Ammonia as an Energy Vector*; Valera-Medina, A.; Bañares-Alcántara, R., Eds.; Elsevier: London, 2020; pp 41–83. https://doi.org/10.1016/B978-0-12-820560-0.00004-7.

(10) Sutton, M. A.; Erisman, J. W.; Dentener, F.; Möller, D. Ammonia in the Environment: From Ancient Times to the Present. *Environ. Pollut.* **2008**, *156* (3), 583–604. https://doi.org/10.1016/j.envpol.2008.03.013.

(11) Watanabe, Y.; Aoki, W.; Ueda, M. Sustainable Biological Ammonia Production towards a Carbon-Free Society. *Sustainability* **2021**, *13* (17), 9496. https://doi.org/10.3390/su13179496.

(12) Yüzbaşıoğlu, A. E.; Avşar, C.; Gezerman, A. O. The Current Situation in the Use of Ammonia as a Sustainable Energy Source and Its Industrial Potential. *Curr. Res. Green Sustain. Chem.* **2022**, *5*, 100307. https://doi.org/10.1016/j.crgsc.2022.100307.

(13) Chai, W. S.; Bao, Y.; Jin, P.; Tang, G.; Zhou, L. A Review on Ammonia, Ammonia-Hydrogen and Ammonia-Methane Fuels. *Renew. Sustain. Energy Rev.* **2021**, *147*, 111254. https://doi.org/10.1016/j.rser.2021.111254.

(14) Valera-Medina, A.; Amer-Hatem, F.; Azad, A. K.; Dedoussi, I. C.; De Joannon, M.; Fernandes, R. X.; Glarborg, P.; Hashemi, H.; He, X.; Mashruk, S.; McGowan, J.; Mounaim-Rouselle, C.; Ortiz-Prado, A.; Ortiz-Valera, A.; Rossetti, I.; Shu, B.; Yehia, M.; Xiao, H.; Costa, M. Review on Ammonia as a Potential Fuel: From Synthesis to Economics. *Energy Fuels* **2021**, *35* (9), 6964–7029. https://doi.org/10.1021/acs.energyfuels.0c03685.

(15) Aziz, M.; Wijayanta, A. T.; Nandiyanto, A. B. D. Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization. *Energies* **2020**, *13* (12), 3062. https://doi.org/10.3390/en13123062.

(16) Zamfirescu, C.; Dincer, I. Ammonia as a Green Fuel and Hydrogen Source for Vehicular Applications. *Fuel Process. Technol.* **2009**, *90* (5), 729–737. https://doi.org/10.1016/j.fuproc.2009.02.004.

(17) Erdemir, D.; Dincer, I. A Perspective on the Use of Ammonia as a Clean Fuel: Challenges and Solutions. *Int. J. Energy Res.* **2021**, *45* (4), 4827–4834. https://doi.org/10.1002/er.6232.

(18) Blois, M. The Industrialization of the Haber-Bosch Process. *C&EN (Chemical & Engineering News)*. 2023. https://cen.acs.org/food/agriculture/The-industrialization-Haber-Bosch-process/101/i26 (accessed 2025-08-07).

(19) Russel, D. A.; Williams, G. G. History of Chemical Fertilizer Development. *Soil Sci. Soc. Am. J.* **1977**, *41* (2), 260–265. https://doi.org/10.2136/sssaj1977.03615995004100020020x.

(20) Cherkasov, N.; Ibhadon, A. O.; Fitzpatrick, P. A Review of the Existing and Alternative Methods for Greener Nitrogen Fixation. *Chem. Eng. Process. Process Intensif.* **2015**, *90*, 24–33. https://doi.org/10.1016/j.cep.2015.02.004.

(21) Pattabathula, V.; Richardson, J. Introduction to Ammonia Production. *CEP Mag*. 2016, Issue 2, pp 69–75.

(22) Tamaru, K. The History of the Development of Ammonia Synthesis. In *Catalytic Ammonia Synthesis*; Jennings, J. R., Ed.; Springer US: Boston, MA, 1991; pp 1–18. https://doi.org/10.1007/978-1-4757-9592-9_1.

(23) Mateo, D.; Sousa, A.; Zakharzhevskii, M.; Gascon, J. Challenges and Opportunities for the Photo-(Thermal) Synthesis of Ammonia. *Green Chem.* **2024**, *26* (3), 1041–1061. https://doi.org/10.1039/D3GC02996D.

(24) Zhou, W.; Zhu, B.; Li, Q.; Ma, T.; Hu, S.; Griffy-Brown, C. CO_2 Emissions and Mitigation Potential in China's Ammonia Industry. *Energy Policy* **2010**, *38* (7), 3701–3709. https://doi.org/10.1016/j.enpol.2010.02.048.

(25) Amhamed, A. I.; Shuibul Qarnain, S.; Hewlett, S.; Sodiq, A.; Abdellatif, Y.; Isaifan, R. J.; Alrebei, O. F. Ammonia Production Plants—A Review. *Fuels* **2022**, *3* (3), 408–435. https://doi.org/10.3390/fuels3030026.

(26) Worrell, E.; Phylipsen, D.; Einstein, D.; Martin, N. *Energy Use and Energy Intensity of the U.S. Chemical Industry*; LBNL--44314, 773773; 2000. https://doi.org/10.2172/773773.

(27) Schlögl, R. Preparation and Activation of the Technical Ammonia Synthesis Catalyst. In *Catalytic Ammonia Synthesis*; Jennings, J. R., Ed.; Springer US: Boston, MA, 1991; pp 19–108. https://doi.org/10.1007/978-1-4757-9592-9_2.

(28) Appl, M. The Haber-Bosch Heritage: The Ammonia Production Technology. In *50th Anniversary of the IFA Technical Conference*; Sevilla, Spain, 1997; Vol. 25, pp 25–26.

(29) Rehman, F.; Delowar Hossain, M.; Tyagi, A.; Lu, D.; Yuan, B.; Luo, Z. Engineering Electrocatalyst for Low-Temperature N_2 Reduction to Ammonia. *Mater. Today* **2021**, *44*, 136–167. https://doi.org/10.1016/j.mattod.2020.09.006.

(30) Højlund Nielsen P.E. Deactivation of Synthetic Catalyst. In *Catalytic Ammonia Synthesis: Fundamentals and Practice*; Jennings, J. R., Ed.; Springer US: Boston, MA, 1991. https://doi.org/10.1007/978-1-4757-9592-9.

(31) Humphreys, J.; Lan, R.; Tao, S. Development and Recent Progress on Ammonia Synthesis Catalysts for Haber–Bosch Process. *Adv. Energy Sustain. Res.* **2021**, *2* (1), 2000043. https://doi.org/10.1002/aesr.202000043.

(32) Gramatica, G.; Pernicone, N. Kinetics of Ammonia Synthesis and Influence on Converter Design. In *Catalytic Ammonia Synthesis*; Jennings, J. R., Ed.; Springer US: Boston, MA, 1991; pp 211–252. https://doi.org/10.1007/978-1-4757-9592-9_6.

(33) Wang, L.; Xia, M.; Wang, H.; Huang, K.; Qian, C.; Maravelias, C. T.; Ozin, G. A. Greening Ammonia toward the Solar Ammonia Refinery. *Joule* **2018**, *2* (6), 1055–1074. https://doi.org/10.1016/j.joule.2018.04.017.

(34) Vojvodic, A.; Medford, A. J.; Studt, F.; Abild-Pedersen, F.; Khan, T. S.; Bligaard, T.; Nørskov, J. K. Exploring the Limits: A Low-Pressure, Low-Temperature Haber–Bosch Process. *Chem. Phys. Lett.* **2014**, *598*, 108–112. https://doi.org/10.1016/j.cplett.2014.03.003.

(35) Dentener, F. J.; Crutzen, P. J. A Three-Dimensional Model of the Global Ammonia Cycle. *J. Atmospheric Chem.* **1994**, *19* (4), 331–369. https://doi.org/10.1007/BF00694492.

(36) Nayak-Luke, R. M.; Cesaro, Z.; Bañares-Alcántara, R. Pathways for Green Ammonia. In *Techno-Economic Challenges of Green Ammonia as an Energy Vector*; Valera-Medina, A.; Bañares-Alcántara, R., Eds.; Elsevier: London, 2020; pp 27–39. https://doi.org/10.1016/B978-0-12-820560-0.00003-5.

(37) Niu, L.; An, L.; Wang, X.; Sun, Z. Effect on Electrochemical Reduction of Nitrogen to Ammonia under Ambient Conditions: Challenges and Opportunities for Chemical Fuels. *J. Energy Chem.* **2021**, *61*, 304–318. https://doi.org/10.1016/j.jechem.2021.01.018.

(38) Smith, C.; Hill, A. K.; Torrente-Murciano, L. Current and Future Role of Haber–Bosch Ammonia in a Carbon-Free Energy Landscape. *Energy Environ. Sci.* **2020**, *13* (2), 331–344. https://doi.org/10.1039/C9EE02873K.

(39) Hatzell, M. C. The Colors of Ammonia. *ACS Energy Lett.* **2024**, *9* (6), 2920–2921. https://doi.org/10.1021/acsenergylett.4c01391.

(40) Nazemi, M.; El-Sayed, M. A. Managing the Nitrogen Cycle via Plasmonic (Photo)Electrocatalysis: Toward Circular Economy. *Acc. Chem. Res.* **2021**, *54* (23), 4294–4304. https://doi.org/10.1021/acs.accounts.1c00446.

(41) Baltrusaitis, J. Sustainable Ammonia Production. *ACS Sustain. Chem. Eng.* **2017**, *5* (11), 9527–9527. https://doi.org/10.1021/acssuschemeng.7b03719.

(42) Hao, D.; Chen, Z.; Figiela, M.; Stepniak, I.; Wei, W.; Ni, B.-J. Emerging Alternative for Artificial Ammonia Synthesis through Catalytic Nitrate Reduction. *J. Mater. Sci. Technol.* **2021**, *77*, 163–168. https://doi.org/10.1016/j.jmst.2020.10.056.

(43) Fu, X.; Zhang, J.; Kang, Y. Recent Advances and Challenges of Electrochemical Ammonia Synthesis. *Chem Catal.* **2022**, *2* (10), 2590–2613. https://doi.org/10.1016/j.checat.2022.09.001.

(44) Han, Y.; Zhang, X.; Cai, W.; Zhao, H.; Zhang, Y.; Sun, Y.; Hu, Z.; Li, S.; Lai, J.; Wang, L. Facet-Controlled Palladium Nanocrystalline for Enhanced Nitrate Reduction towards Ammonia. *J. Colloid Interface Sci.* **2021**, *600*, 620–628. https://doi.org/10.1016/j.jcis.2021.05.061.

(45) Wei, P.; Liang, J.; Liu, Q.; Xie, L.; Tong, X.; Ren, Y.; Li, T.; Luo, Y.; Li, N.; Tang, B.; Asiri, A. M.; Hamdy, M. S.; Kong, Q.; Wang, Z.; Sun, X. Iron-Doped Cobalt Oxide Nanoarray for Efficient Electrocatalytic Nitrate-to-Ammonia Conversion. *J. Colloid Interface Sci.* **2022**, *615*, 636–642. https://doi.org/10.1016/j.jcis.2022.01.186.

(46) Yang, S.; Wang, X.; Song, Z.; Liu, C.; Li, Z.; Wang, J.; Song, L. Efficient Electrocatalytic Nitrate Reduction in Neutral Medium by Cu/CoP/NF Composite Cathode Coupled with Ir-Ru/Ti Anode. *Chemosphere* **2022**, *307*, 136132. https://doi.org/10.1016/j.chemosphere.2022.136132.

(47) Fu, X.; Zhao, X.; Hu, X.; He, K.; Yu, Y.; Li, T.; Tu, Q.; Qian, X.; Yue, Q.; Wasielewski, M. R.; Kang, Y. Alternative Route for Electrochemical Ammonia Synthesis by Reduction of Nitrate on Copper Nanosheets. *Appl. Mater. Today* **2020**, *19*, 100620. https://doi.org/10.1016/j.apmt.2020.100620.

(48) Ren, Z.; Chen, Q.; Zhang, J.; An, X.; Liu, Q.; Xie, L.; Yao, W.; Sun, X.; Kong, Q. Electrodeposited Ni-Mo-P Nanoparticles on TiO_2 Nanoribbon Array for Electrocatalytic Ammonia Synthesis by Reducing Nitrite. *Mater. Today Phys.* **2023**, *36*, 101162. https://doi.org/10.1016/j.mtphys.2023.101162.

(49) Li, Y.; Xiao, S.; Li, X.; Chang, C.; Xie, M.; Xu, J.; Yang, Z. A Robust Metal-Free Electrocatalyst for Nitrate Reduction Reaction to Synthesize Ammonia. *Mater. Today Phys.* **2021**, *19*, 100431. https://doi.org/10.1016/j.mtphys.2021.100431.

(50) Liu, Q.; Wen, G.; Zhao, D.; Xie, L.; Sun, S.; Zhang, L.; Luo, Y.; Ali Alshehri, A.; Hamdy, M. S.; Kong, Q.; Sun, X. Nitrite Reduction over Ag Nanoarray Electrocatalyst for Ammonia Synthesis. *J. Colloid Interface Sci.* **2022**, *623*, 513–519. https://doi.org/10.1016/j.jcis.2022.04.173.

(51) Wang, J.; Feng, J.; Soyol-Erdene, T.-O.; Wei, Z.; Tang, W. Electrodeposited NiCoP on Nickel Foam as a Self-Supported Cathode for Highly Selective Electrochemical Reduction of Nitrate to Ammonia. *Sep. Purif. Technol.* **2023**, *320*, 124155. https://doi.org/10.1016/j.seppur.2023.124155.

(52) Deng, Z.; Ma, C.; Fan, X.; Li, Z.; Luo, Y.; Sun, S.; Zheng, D.; Liu, Q.; Du, J.; Lu, Q.; Zheng, B.; Sun, X. Construction of CoP/TiO_2 Nanoarray for Enhanced Electrochemical Nitrate Reduction to Ammonia. *Mater. Today Phys.* **2022**, *28*, 100854. https://doi.org/10.1016/j.mtphys.2022.100854.

(53) Li, Z.; Liang, J.; Liu, Q.; Xie, L.; Zhang, L.; Ren, Y.; Yue, L.; Li, N.; Tang, B.; Alshehri, A. A.; Hamdy, M. S.; Luo, Y.; Kong, Q.; Sun, X. High-Efficiency Ammonia Electrosynthesis via Selective Reduction of Nitrate on $ZnCo_2O_4$ Nanosheet Array. *Mater. Today Phys.* **2022**, *23*, 100619. https://doi.org/10.1016/j.mtphys.2022.100619.

(54) Zhang, X.; Wang, Y.; Liu, C.; Yu, Y.; Lu, S.; Zhang, B. Recent Advances in Non-Noble Metal Electrocatalysts for Nitrate Reduction. *Chem. Eng. J.* **2021**, *403*, 126269. https://doi.org/10.1016/j.cej.2020.126269.

(55) Giddey, S.; Badwal, S. P. S.; Kulkarni, A. Review of Electrochemical Ammonia Production Technologies and Materials. *Int. J. Hydrog. Energy* **2013**, *38* (34), 14576–14594. https://doi.org/10.1016/j.ijhydene.2013.09.054.

(56) Kyriakou, V.; Garagounis, I.; Vasileiou, E.; Vourros, A.; Stoukides, M. Progress in the Electrochemical Synthesis of Ammonia. *Catal. Today* **2017**, *286*, 2–13. https://doi.org/10.1016/j.cattod.2016.06.014.

(57) Zhao, R.; Xie, H.; Chang, L.; Zhang, X.; Zhu, X.; Tong, X.; Wang, T.; Luo, Y.; Wei, P.; Wang, Z.; Sun, X. Recent Progress in the Electrochemical Ammonia Synthesis under Ambient Conditions. *EnergyChem* **2019**, *1* (2), 100011. https://doi.org/10.1016/j.enchem.2019.100011.

(58) Lei, Z.; Jing, J.; Pang, J.; Hu, R.; Shi, X.; Yang, Z.; Peng, S. Highly Conductive Proton-Conducting Electrolyte with a Low Sintering Temperature for Electrochemical Ammonia Synthesis. *Int. J. Hydrog. Energy* **2020**, *45* (15), 8041–8051. https://doi.org/10.1016/j.ijhydene.2020.01.039.

(59) Marnellos, G.; Stoukides, M. Ammonia Synthesis at Atmospheric Pressure. *Science* **1998**, *282* (5386), 98–100. https://doi.org/10.1126/science.282.5386.98.

(60) Yang, C.; Zhu, Y.; Liu, J.; Qin, Y.; Wang, H.; Liu, H.; Chen, Y.; Zhang, Z.; Hu, W. Defect Engineering for Electrochemical Nitrogen Reduction Reaction to Ammonia. *Nano Energy* **2020**, *77*, 105126. https://doi.org/10.1016/j.nanoen.2020.105126.

(61) Kim, H.; Chung, Y. S.; Kim, T.; Yoon, H.; Sung, J. G.; Jung, H. K.; Kim, W. B.; Sammes, L. B.; Chung, J. S. Ru-Doped Barium Strontium Titanates of the Cathode for the Electrochemical Synthesis of Ammonia. *Solid State Ion.* **2019**, *339*, 115010. https://doi.org/10.1016/j.ssi.2019.115010.

(62) Li, L.; Tang, C.; Jin, H.; Davey, K.; Qiao, S.-Z. Main-Group Elements Boost Electrochemical Nitrogen Fixation. *Chem* **2021**, *7* (12), 3232–3255. https://doi.org/10.1016/j.chempr.2021.10.008.

(63) Amar, I. A.; Lan, R.; Humphreys, J.; Tao, S. Electrochemical Synthesis of Ammonia from Wet Nitrogen via a Dual-Chamber Reactor Using $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-$Ce_{0.8}Gd0.18Ca_{0.02}O_{2-\delta}$ Composite Cathode. *Catal. Today* **2017**, *286*, 51–56. https://doi.org/10.1016/j.cattod.2016.09.006.

(64) Li, Z.; Li, M.; Yang, J.; Liao, M.; Song, G.; Cao, J.; Liu, F.; Wang, Z.; Kawi, S.; Lin, Q. Electrocatalyst Design Strategies for Ammonia Production via N_2 Reduction. *Catal. Today* **2022**, *388–389*, 12–25. https://doi.org/10.1016/j.cattod.2021.06.008.

(65) Guo, D.; Wang, S.; Xu, J.; Zheng, W.; Wang, D. Defect and Interface Engineering for Electrochemical Nitrogen Reduction Reaction under Ambient Conditions. *J. Energy Chem.* **2022**, *65*, 448–468. https://doi.org/10.1016/j.jechem.2021.06.012.

(66) Liu, Q.; Xu, T.; Luo, Y.; Kong, Q.; Li, T.; Lu, S.; Alshehri, A. A.; Alzahrani, K. A.; Sun, X. Recent Advances in Strategies for Highly Selective Electrocatalytic N_2 Reduction toward Ambient NH_3 Synthesis. *Curr. Opin. Electrochem.* **2021**, *29*, 100766. https://doi.org/10.1016/j.coelec.2021.100766.

(67) Fasihi, M.; Weiss, R.; Savolainen, J.; Breyer, C. Global Potential of Green Ammonia Based on Hybrid PV-Wind Power Plants. *Appl. Energy* **2021**, *294*, 116170. https://doi.org/10.1016/j.apenergy.2020.116170.

(68) Erfani, N.; Baharudin, L.; Watson, M. Recent Advances and Intensifications in Haber-Bosch Ammonia Synthesis Process. *Chem. Eng. Process. - Process Intensif.* **2024**, *204*, 109962. https://doi.org/10.1016/j.cep.2024.109962.

(69) Cheema, I. I.; Krewer, U. Operating Envelope of Haber–Bosch Process Design for Power-to-Ammonia. *RSC Adv.* **2018**, *8* (61), 34926–34936. https://doi.org/10.1039/C8RA06821F.

(70) Ozturk, M.; Dincer, I. An Integrated System for Ammonia Production from Renewable Hydrogen: A Case Study. *Int. J. Hydrog. Energy* **2021**, *46* (8), 5918–5925. https://doi.org/10.1016/j.ijhydene.2019.12.127.

(71) El-Shafie, M.; Kambara, S. Recent Advances in Ammonia Synthesis Technologies: Toward Future Zero Carbon Emissions. *Int. J. Hydrog. Energy* **2023**, *48* (30), 11237–11273. https://doi.org/10.1016/j.ijhydene.2022.09.061.

(72) Ribeiro, C.; Santos, D. M. F. Transitioning Ammonia Production: Green Hydrogen-Based Haber–Bosch and Emerging Nitrogen Reduction Technologies. *Clean Technol.* **2025**, *7* (2), 49. https://doi.org/10.3390/cleantechnol7020049.

(73) Bora, N.; Kumar Singh, A.; Pal, P.; Kumar Sahoo, U.; Seth, D.; Rathore, D.; Bhadra, S.; Sevda, S.; Venkatramanan, V.; Prasad, S.; Singh, A.; Kataki, R.; Kumar Sarangi, P. Green Ammonia Production: Process Technologies and Challenges. *Fuel* **2024**, *369*, 131808. https://doi.org/10.1016/j.fuel.2024.131808.

(74) Frattini, D.; Cinti, G.; Bidini, G.; Desideri, U.; Cioffi, R.; Jannelli, E. A System Approach in Energy Evaluation of Different Renewable Energies Sources Integration in Ammonia Production Plants. *Renew. Energy* **2016**, *99*, 472–482. https://doi.org/10.1016/j.renene.2016.07.040.

(75) Allman, A.; Daoutidis, P. Optimal Scheduling for Wind-Powered Ammonia Generation: Effects of Key Design Parameters. *Chem. Eng. Res. Des.* **2018**, *131*, 5–15. https://doi.org/10.1016/j.cherd.2017.10.010.

(76) Wang, C.; Walsh, S. D. C.; Longden, T.; Palmer, G.; Lutalo, I.; Dargaville, R. Optimising Renewable Generation Configurations of Off-Grid Green Ammonia Production Systems Considering Haber-Bosch Flexibility. *Energy Convers. Manag.* **2023**, *280*, 116790. https://doi.org/10.1016/j.enconman.2023.116790.

(77) Wen, D.; Aziz, M. Flexible Operation Strategy of an Integrated Renewable Multi-Generation System for Electricity, Hydrogen, Ammonia, and Heating. *Energy Convers. Manag.* **2022**, *253*, 115166. https://doi.org/10.1016/j.enconman.2021.115166.

(78) Osman, O.; Sgouridis, S.; Sleptchenko, A. Scaling the Production of Renewable Ammonia: A Techno-Economic Optimization Applied in Regions with High Insolation. *J. Clean. Prod.* **2020**, *271*, 121627. https://doi.org/10.1016/j.jclepro.2020.121627.

(79) Lianos, P. Review of Recent Trends in Photoelectrocatalytic Conversion of Solar Energy to Electricity and Hydrogen. *Appl. Catal. B Environ.* **2017**, *210*, 235–254. https://doi.org/10.1016/j.apcatb.2017.03.067.

(80) Li, R. Photocatalytic Nitrogen Fixation: An Attractive Approach for Artificial Photocatalysis. *Chin. J. Catal.* **2018**, *39* (7), 1180–1188. https://doi.org/10.1016/S1872-2067(18)63104-3.

(81) Shen, H.; Yang, M.; Hao, L.; Wang, J.; Strunk, J.; Sun, Z. Photocatalytic Nitrogen Reduction to Ammonia: Insights into the Role of Defect Engineering in Photocatalysts. *Nano Res.* **2022**, *15* (4), 2773–2809. https://doi.org/10.1007/s12274-021-3725-0.

(82) Huang, H.; Wang, X.-S.; Philo, D.; Ichihara, F.; Song, H.; Li, Y.; Li, D.; Qiu, T.; Wang, S.; Ye, J. Toward Visible-Light-Assisted Photocatalytic Nitrogen Fixation: A Titanium Metal Organic Framework with Functionalized Ligands. *Appl. Catal. B Environ.* **2020**, *267*, 118686. https://doi.org/10.1016/j.apcatb.2020.118686.

(83) Meng, S.-L.; Li, X.-B.; Tung, C.-H.; Wu, L.-Z. Nitrogenase Inspired Artificial Photosynthetic Nitrogen Fixation. *Chem* **2021**, *7* (6), 1431–1450. https://doi.org/10.1016/j.chempr.2020.11.002.

(84) Rapson, T. D.; Gregg, C. M.; Allen, R. S.; Ju, H.; Doherty, C. M.; Mulet, X.; Giddey, S.; Wood, C. C. Insights into Nitrogenase Bioelectrocatalysis for Green Ammonia Production. *ChemSusChem* **2020**, *13* (18), 4856–4865. https://doi.org/10.1002/cssc.202001433.

(85) Smith, B. E. Structure, Function, and Biosynthesis of the Metallosulfur Clusters in Nitrogenases. *Adv. Inorg. Chem* **1999**, 47, pp 159–218. https://doi.org/10.1016/S0898-8838(08)60078-1.

(86) Watanabe, Y.; Aoki, W.; Ueda, M. Ammonia Production Using Bacteria and Yeast toward a Sustainable Society. *Bioengineering* **2023**, *10* (1), 82. https://doi.org/10.3390/bioengineering10010082.

(87) Bennett, E. M.; Murray, J. W.; Isalan, M. Engineering Nitrogenases for Synthetic Nitrogen Fixation: From Pathway Engineering to Directed Evolution. *BioDesign Res.* **2023**, *5*, 0005. https://doi.org/10.34133/bdr.0005.

(88) Newton, W. E. Physiology, Biochemistry, and Molecular Biology of Nitrogen Fixation. In *Biology of the Nitrogen Cycle*; Bothe, H.; Ferguson, S. J.; Newton, W. E., Eds.; Elsevier: Amsterdam, 2007; pp 109–129. https://doi.org/10.1016/B978-044452857-5.50009-6.

(89) Hoffman, B. M.; Lukoyanov, D.; Yang, Z.-Y.; Dean, D. R.; Seefeldt, L. C. Mechanism of Nitrogen Fixation by Nitrogenase: The Next Stage. *Chem. Rev.* **2014**, *114* (8), 4041–4062. https://doi.org/10.1021/cr400641x.

(90) Beringer, J. E.; Hirsch, P. R. Genetic Engineering and Nitrogen Fixation. *Biotechnol. Genet. Eng. Rev.* **1984**, *1* (1), 65–88. https://doi.org/10.1080/02648725.1984.10647781.

(91) Waite, C. J.; Lindström Battle, A.; Bennett, M. H.; Carey, M. R.; Hong, C. K.; Kotta-Loizou, I.; Buck, M.; Schumacher, J. Resource Allocation During the Transition to Diazotrophy in *Klebsiella Oxytoca*. *Front. Microbiol.* **2021**, *12*, 718487. https://doi.org/10.3389/fmicb.2021.718487.

(92) Li, X.-X.; Liu, Q.; Liu, X.-M.; Shi, H.-W.; Chen, S.-F. Using Synthetic Biology to Increase Nitrogenase Activity. *Microb. Cell Factories* **2016**, *15* (1), 43. https://doi.org/10.1186/s12934-016-0442-6.

(93) Wang, D.; Xu, A.; Elmerich, C.; Ma, L. Z. Biofilm Formation Enables Free-Living Nitrogen-Fixing Rhizobacteria to Fix Nitrogen under Aerobic Conditions. *ISME J.* **2017**, *11* (7), 1602–1613. https://doi.org/10.1038/ismej.2017.30.

(94) Takimoto, R.; Tatemichi, Y.; Aoki, W.; Kosaka, Y.; Minakuchi, H.; Ueda, M.; Kuroda, K. A Critical Role of an Oxygen-Responsive Gene for Aerobic Nitrogenase Activity in *Azotobacter Vinelandii* and Its Application to *Escherichia Coli*. *Sci. Rep.* **2022**, *12* (1), 4182. https://doi.org/10.1038/s41598-022-08007-4.

(95) Burén, S.; Jiang, X.; López-Torrejón, G.; Echavarri-Erasun, C.; Rubio, L. M. Purification and In Vitro Activity of Mitochondria Targeted Nitrogenase Cofactor Maturase NifB. *Front. Plant Sci.* **2017**, *8*, 1567. https://doi.org/10.3389/fpls.2017.01567.

(96) Burén, S.; Pratt, K.; Jiang, X.; Guo, Y.; Jimenez-Vicente, E.; Echavarri-Erasun, C.; Dean, D. R.; Saaem, I.; Gordon, D. B.; Voigt, C. A.; Rubio, L. M. Biosynthesis of the Nitrogenase Active-Site Cofactor Precursor NifB-Co in *Saccharomyces Cerevisiae*. *Proc. Natl. Acad. Sci. U.S.A* **2019**, *116* (50), 25078–25086. https://doi.org/10.1073/pnas.1904903116.

(97) Chrétien, D.; Bénit, P.; Ha, H.-H.; Keipert, S.; El-Khoury, R.; Chang, Y.-T.; Jastroch, M.; Jacobs, H. T.; Rustin, P.; Rak, M. Mitochondria Are Physiologically Maintained at Close to 50 °C. *PLOS Biol.* **2018**, *16* (1), e2003992. https://doi.org/10.1371/journal.pbio.2003992.

(98) Ueda, M.; Tanaka, A. Cell Surface Engineering of Yeast: Construction of Arming Yeast with Biocatalyst. *J. Biosci. Bioeng.* **2000**, *90* (2), 125–136.

(99) Watanabe, Y.; Kuroda, K.; Tatemichi, Y.; Nakahara, T.; Aoki, W.; Ueda, M. Construction of Engineered Yeast Producing Ammonia from Glutamine and Soybean Residues (Okara). *AMB Express* **2020**, *10* (1), 70. https://doi.org/10.1186/s13568-020-01011-9.

(100) Milton, R. D.; Cai, R.; Abdellaoui, S.; Leech, D.; De Lacey, A. L.; Pita, M.; Minteer, S. D. Bioelectrochemical Haber–Bosch Process: An Ammonia-Producing H_2 /N_2 Fuel Cell. *Angew. Chem. Int. Ed.* **2017**, *56* (10), 2680–2683. https://doi.org/10.1002/anie.201612500.

(101) Brown, K. A.; Harris, D. F.; Wilker, M. B.; Rasmussen, A.; Khadka, N.; Hamby, H.; Keable, S.; Dukovic, G.; Peters, J. W.; Seefeldt, L. C.; King, P. W. Light-Driven Dinitrogen Reduction Catalyzed by a CdS:Nitrogenase MoFe Protein Biohybrid. *Science* **2016**, *352* (6284), 448–450. https://doi.org/10.1126/science.aaf2091.

(102) Dent, D.; Cocking, E. Establishing Symbiotic Nitrogen Fixation in Cereals and Other Non-Legume Crops: The Greener Nitrogen Revolution. *Agric. Food Secur.* **2017**, *6* (1), 7. https://doi.org/10.1186/s40066-016-0084-2.

(103) Li, X.-X.; Liu, Q.; Liu, X.-M.; Shi, H.-W.; Chen, S.-F. Using Synthetic Biology to Increase Nitrogenase Activity. *Microb. Cell Factories* **2016**, *15* (1), 43. https://doi.org/10.1186/s12934-016-0442-6.