

Techno-economic analysis and life cycle assessment for electrochemical ammonia production using proton conducting membrane

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ABSTRACT Green ammonia production is facing increasing interest on a global scale as a hydrogen carrier for power generation as well as fertilizer for food production. The conventional Haber-Bosch method for ammonia synthesis is energy demanding, requires high purity hydrogen, and is based on fossil fuels. A preliminary techno-economic model for electrochemical ammonia synthesis at near ambient pressure using feed rates of 32 metric ton/day for hydrogen and 135 metric ton/day for nitrogen is presented in this study. Various

pathways using different methods for nitrogen generation and hydrogen production were investigated to gain insight into added energy savings per metric ton of ammonia. Electrochemical synthesis using electrolysis for hydrogen and cryogenic nitrogen was found to be a potentially viable pathway for green ammonia. The profitability metrics including discounted cash flow rate of return, net present value and discounted payback period were estimated to be 8%, \$40 MM, and 4 to 6 years respectively for this pathway. The cost of electricity, conversion rate, and conversion efficiency dominate the tonnage cost of ammonia and were used to assess the feasibility of the model. A life cycle assessment was also conducted to assess the environmental impact of a well to product ammonia process.

Introduction

Ammonia is a trigonal pyramidal compound comprising diatomic nitrogen and hydrogen molecules. It can exist as a vapor at standard temperature and pressure or liquid phase at high pressure (compressed) and low temperature (cooled). The gravimetric energy density, 3 kW. kg⁻¹, [1] is higher and cost to transport as well as distribute is comparatively lower to hydrogen. [2] It is carbon-free [2,3] and has many applications in the chemical processing industry where it is commercially used as nitrogen fertilizer. It is also an excellent hydrogen carrier [3–5] and used as a clean fuel. [6,7] In the ammonia economy, it can be implemented as a renewable fuel in carbon neutral vehicular transportation due to ease of on board storage in vehicles and it is less expensive to distribute by pipeline when compared to hydrogen. [8,9] Ammonia is commonly produced by the Haber-Bosch (H-B) process developed in the 20th century by chemists, Fritz Haber and Carl Bosch. [10] Intense catalysis research [11–20] is still ongoing for this method of manufacturing ammonia which uses hydrogen produced by steam methane reforming and is not

fossil free.[21,22] It is known, large-scale centralized H-B technology is energy demanding[23] in its use of high temperatures [400-500 °C][1] to maintain fast reaction rates and high pressures [150-250 bar][1] which maintains the equilibrium position to the right based on Le Chatelier's principle. On the other hand, there is recent research effort[13,17,18] towards small-scale H-B to lessen the severe operating conditions and achieve renewable power but it encounters many challenges. These challenges span catalyst performance, reaction conditions, constant reactant and energy inputs, product yield and more to remain economical.[14,24–26] Electrochemical ammonia synthesis from water and air at low temperatures (≤ 200 °C) is renewable with no carbon dioxide (CO₂) emissions and can address the challenges aforementioned in its use of less severe operating conditions, increased yield as well as attractiveness for variable production. Progress in mild electrochemical synthesis of ammonia is ongoing and the area has gained research momentum particularly with regards to electrolytes, electro-catalysts and cell configuration to improve reaction rates and efficiencies.[21–23,27–36] As research work proceeds to improve these critical process parameters, there is a need to simultaneously have insight into the financial metrics of ammonia synthesis. Techno-economic studies have been carried out for the integration of reactant pathways including air separation for nitrogen generation and steam reforming for hydrogen production from natural gas and coal with the H-B synthesis loop process.[25,37,38] Although these studies review processes integrated for the existing H-B technology, alternative cost-effective and energy-efficient ammonia synthesis methods should also be analyzed. Additionally, life cycle assessment (LCA) is an important tool to analyze the cradle to grave environmental impact of production methods for products like ammonia and has been defined by the International Organization for Standardization (ISO) 14040 and 14044. LCA has been carried out for the Haber-Bosch and electrolysis process

combined with various power plant types including hydropower, biomass, nuclear and municipal waste. The overall environmental footprint can be reduced with renewable resources and can replace the centralized ammonia production plants that are fossil fuel based.[39–41] To the best of the authors' knowledge, there is no study focusing on the effort to effectively assess various hydrogen and nitrogen processes for electrochemical ammonia synthesis for potentially lower energy consumption. Therefore, this study focuses on a preliminary sensitivity analysis developed to understand the early stage economic implications and life cycle assessment for the electrochemical synthesis of ammonia. There is no existing commercial plant and model information has been obtained from the literature as well as industry experts. The pathways for producing hydrogen and generating nitrogen in combination with electrochemical synthesis have also been evaluated. Additionally, studies were carried out to determine the variation in the net present value (NPV) and discounted payback period (DPBP) with price of electricity. The price of electricity is one of the important parameters which can direct the success of medium-scale, mild electrochemical ammonia synthesis.

Methodology

Market Survey

Uncertainty factors including feedstock market, customer demands, and regulatory pressures influence economic profitability in the chemical industry. World ammonia production is expected to grow by 6% within the next three years. Table 1 shows production of ammonia by top exporting countries in the year 2017.[42]

Table 1: Top ammonia producing countries and largest importers (adapted from Massachusetts Institute of Technology's Observatory of Economic Complexity tool).[43]

Top Country to/Top Country from	Origin Country Annual Production (MM\$/ MMT)
United States of America/Trinidad & Tobago	965/4.9
Ukraine/Russia	789/13.0
United States of America /Canada	467/4.1
South Korea/Saudi Arabia	456/4.1
Spain/Algeria	426/1.2

The change in demand is attributed to regions such as Latin America because of sustainability efforts and acreage expansions.

Site Selection

The selection of the plant location influences the project costs and profitability. For this techno-economic model, it was assumed the ammonia electrochemical plant is within close proximity in the U.S. to the supply of renewable raw materials and the market for the sale of ammonia. Currently, 60 % of ammonia production in the U.S. takes place in South Central United States. The modular design capability via the electrochemical method will allow operation on a small scale without intermediate hydrogen feed.

Process simulation

The ammonia synthesis simulation was carried out using the chemical process simulator,[44] Aspen Plus™ V10. Mass and energy flows were carried out using Aspen Plus™ software package to establish the techno-economic analysis. Figure 1 shows the process flow diagram for the electrochemical synthesis of ammonia.

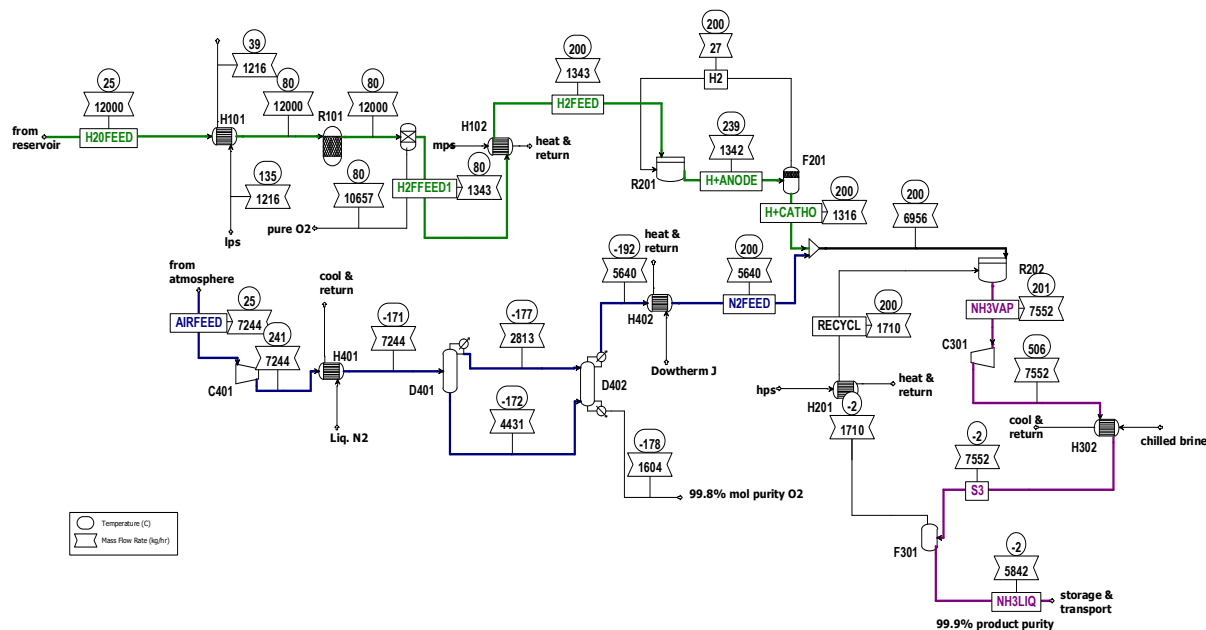
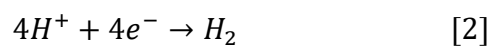
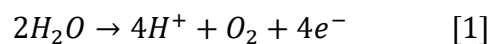


Figure 1: Process flow diagram for the electrochemical synthesis of ammonia

The ELECNRTL which is a combined activity coefficient and equation of state property model was selected in Aspen Plus™ and used to predict the phase behavior for the solid polymer electrolyte system. All the major components including nitrogen, hydrogen, and ammonia as well as their associated chemical and physical properties were found within the vast Aspen Plus™ property database. Real gas approximations were used for all gases. The model assumptions included electrolysis grade feed water, high purity hydrogen and nitrogen feed gases as > 99% with trace levels of moisture and oxygen, at least 85% efficiency for electrolysis-based hydrogen production, stoichiometric air, and 90% efficiency for nitrogen capture across all examined methods. All heat exchangers are simulated as Tubular Exchanger Manufacturers Association (TEMA) shell and tube. Compressors are assumed ASME isentropic as the heat losses are not modeled, centrifugal type and horizontal. Distillation columns use horizontal drum design for condensers and kettle type reboiler. The NRR Faradaic efficiency in the

electrochemical model was taken to be a fixed point at 80% based on recent research where values as high as 56 % with $1.22 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$ [45] have been achieved compared to the DOE target of 90% with $9.3 \times 10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$. Offsite utilities and other outside battery limit (OSBL) parameters including plant access and safety equipment were not modeled explicitly, but were included in the cost evaluation.

The electrochemical ammonia synthesis starts out with models for hydrogen production and nitrogen capture. Hydrogen production by low temperature ($T= 80^\circ\text{C}$) electrolysis is shown in Figure 2. The technology, both alkaline and acidic types, come with challenges including long-term stability of electrode materials and cross permeation of gases.[46] Low temperature electrolysis was assumed because of the known reduced cost when compared to high temperature electrolysis despite the greater than 90% efficiencies achieved in the latter. A 288 metric ton/day ambient water feed is heated to 80°C in a 4- shell and tube heat exchanger, H-101 using low pressure steam (lps) as the utility before being sent to the reactor (0.8 m by diameter), R-101, a stoichiometry-based (RSTOIC) block used to define a conversion value 1, for the following series of reactions occurs:



The diameter of R-101 was found to be 0.8 m. The standard enthalpy for the water splitting reaction to produce hydrogen is 286 kJ per mole. The energy demand for this low temperature electrolysis scenario is at least 40 MWh per metric ton hydrogen with over 80% from electricity use. A component separator block, is then used to simulate the 32 metric ton/day of hydrogen gas leaving the cathode and oxygen leaving from the anode. The oxygen is assumed to be further

processed to liquid then stored and sold. The processing of oxygen is not accounted for in the model.

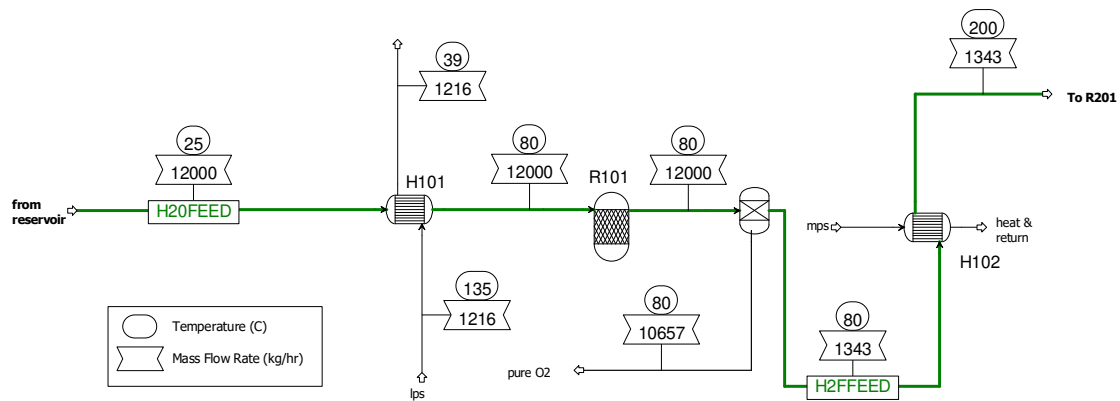


Figure 2: A model for the hydrogen generation process by low temperature electrolysis

The gaseous hydrogen is then heated to 200 °C via the heat exchanger, H-102, using medium pressure steam (mps) utility.

Next, a 173 metric ton/day stoichiometric air feed is directed to an air separation unit where cryogenic distillation takes place to capture 135 metric ton/day nitrogen gas as shown in Figure 3. A cryogenic process was selected for the nitrogen generation simulation because of high volume capacity upwards of 5000 Nm³/h and mass purities for gas products greater than 99%. In C-401 ($P_{\text{initial}}=\text{ambient}$, $P_{\text{final}}=6.5$ bar, net power = 2117 kW), the air stream is compressed from ambient pressure to 6.5 bar before being cooled to -171 °C in H-401. This stream enters a classical two-column (60 stages each) cryogenic distillation setup, D-401 and D-402, to allow nitrogen and oxygen separation. A total condenser is used and a reboiler is not present on the first column (54 m for tangent to tangent height, 0.6 m in diameter). A partial-vapor condenser is used in the second column (55 m for tangent to tangent height, 0.6 m in diameter). In the first

column, the top stream is pure nitrogen and the bottom stream is a mixed stream of oxygen and nitrogen. Both streams

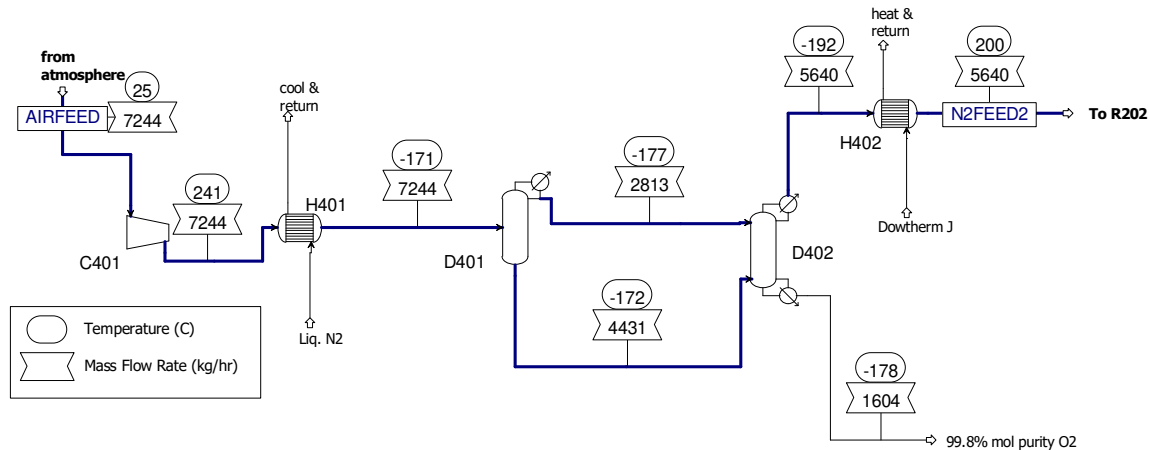


Figure 3: A model for nitrogen generation via an air separation unit based on cryogenic distillation conditions with the product leaving the process as a vapor phase.

enter the second column for further separation to give 135 metric ton/day nitrogen vapor distillate with >99% mole purity that is heated to 200 °C using Dowtherm A utility in H-402. The minimum energy requirements for this cryogenic process is at least 0.4 MWh per metric ton of nitrogen.

A survey of the literature for medium to low temperature electrochemical ammonia synthesis reveals temperature ranges from 200 °C for molten hydroxide electrolytes[47,48] to 80 °C and below for polymer based[49–52] and liquid electrolytes[53–57]. The highest ammonia formation rate has been reported up to $10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$. The hydrogen and nitrogen gaseous feeds enter at the operating conditions of the electrochemical reactor, 200 °C and ambient pressure, which is modeled in this work as a combination of system blocks. The combined

blocks primarily include two batch reactors, R-201 (anode, 0.2 m by diameter) and R-202 (cathode, 0.2 m by diameter), as well as a vertical (0.9 m by diameter) flash drum, F-201 (proton-conducting solid or composite membrane). Both reactors were simulated using the conversion of hydrogen to monitor the reaction. R-201 The 32 metric ton/day hydrogen feed enters the anode, R-201, from H-102 as shown in Figure 4.

The following anode reaction occurs:

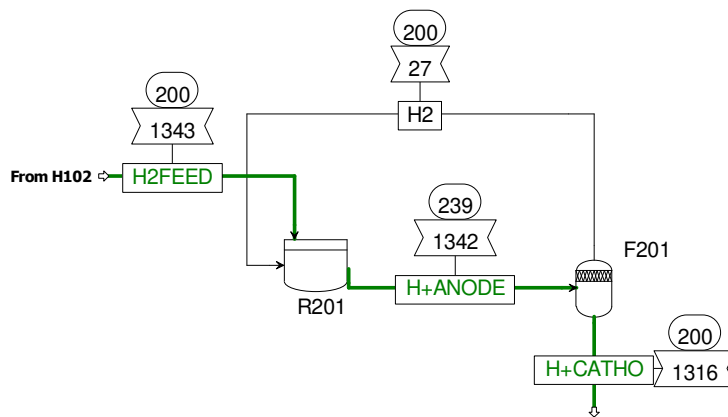
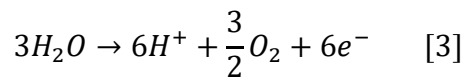


Figure 4: Anode compartment of the electrochemical cell with proton conducting membrane.

The H⁺ ions generated in the anode compartment migrate through the proton conducting membrane to the cathode side shown in Figure 5. The total solid or composite membrane area needed was estimated to be 11 m² based on process time and efficiency of the membrane is assumed to be > 97%.

The cathode side of the electrochemical cell is shown in Figure 5. The H⁺ ions from F-201 react with the 135 metric ton/day nitrogen feed from H-402 to form gaseous ammonia in R-202, according to the following cathode reaction:

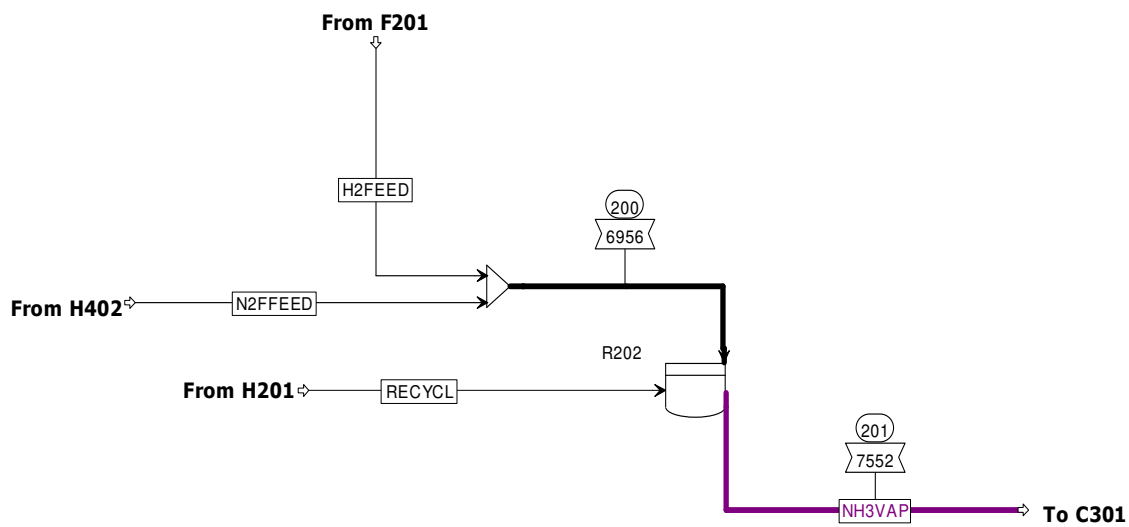
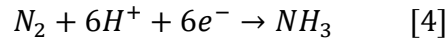


Figure 5: Cathode compartment of the electrochemical cell complete with reactant recycle

140 metric ton/day gaseous ammonia is produced assuming 83% Faradaic efficiency and $9.3 \times 10^7 \text{ mol s}^{-1} \text{ cm}^{-2}$ ammonia formation rate from the Advanced Research Projects Agency–Energy (ARPA-E) Renewable Energy to Fuels Through Utilization of Energy-Dense Liquids (REFUEL) program at the U.S. Department of Energy (DOE). Unused reactants from H-201 return to the cathode, R-202 at cell operating conditions, 200 °C and ambient pressure. The energy demand for the electrochemical synthesis is estimated to be at least 8 MWh per metric ton ammonia. The daily product rate of approximately 140 metric ton gaseous ammonia with 99% mole purity is then compressed in C-301 ($P_{\text{initial}}=\text{ambient}$, $P_{\text{final}}=11 \text{ bar}$, net power = 2117 kW) and cooled in H-301 ($T_{\text{initial}}=506 \text{ °C}$, $T_{\text{final}}=-2 \text{ °C}$) before entering a flash drum, F-301 to produce liquid ammonia

as shown in Figure 6. A second vertical (1 m by diameter) flash drum, F-301, is used to generate the final product at -2 °C and 11 bar corresponding to a density of 641 kg/m³ for the liquid ammonia. Unreacted nitrogen and hydrogen are then recycled and heated in H-201, to the normal operating conditions of the electrochemical cell. The estimated energy demand for ammonia liquefaction is 0.9 MWh per metric ton of ammonia based on Aspen Plus simulation results.

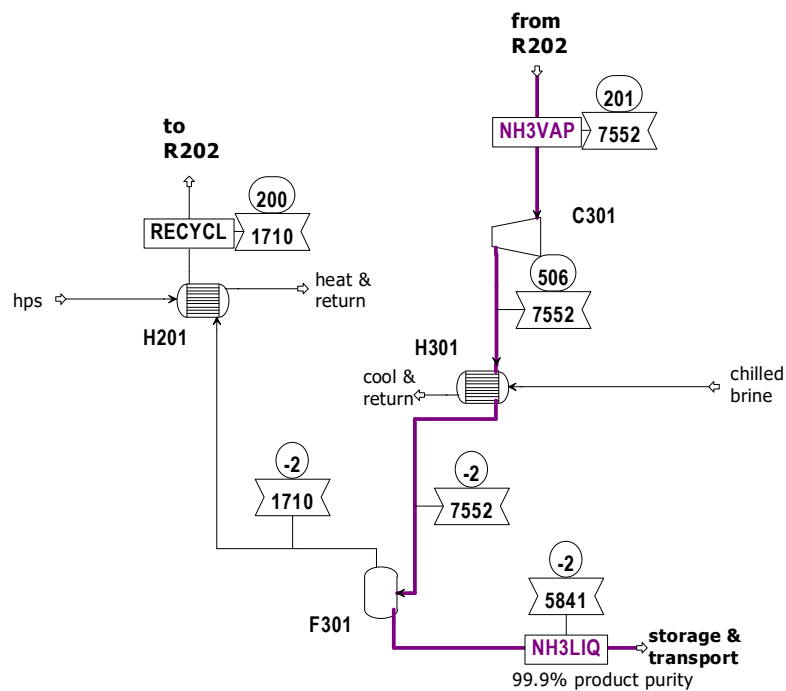


Figure 6: Conditioning of the gaseous ammonia to liquid ammonia product.

The total estimated energy requirements for the electrochemical synthesis of ammonia from hydrogen produced by electrolysis and nitrogen generated by cryogenic distillation along with its separation and liquefaction is at least 15 MWh per metric ton of ammonia. The energy consumption for water splitting is the most energy demanding module in the process. When applied in practice, losses are expected and the energy requirement will be higher.

Techno-Economic Analysis for Electrochemical Ammonia Synthesis

The economic assumptions include a small plant capacity of 140 metric ton ammonia per day and stream factor of 0.96 or 350 days per year. All dollars refer to the U.S. dollars or USD. A 75 MW capacity plant is modeled with a 20-year plant life. The capital investment is assumed to be 100% equity and economic analysis carried out at an internal rate of return of 8%. A corporate tax-rate of 35% and depreciation of cash flow by Maximum Accelerated Cost Recovery System (MACRS) 5-year recovery period for a class life of 9.5 years for manufacturing of chemicals were used. The cost estimate considers all major equipment within the battery limit and is considered early preliminary with a range of uncertainty $\pm 15\text{-}25\%$. Land cost, working capital and salvage value were approximated as 10% of the fixed capital cost. All cash flows include the time value of money and are discounted. The cost of chemicals was adjusted to future prices at the real interest rate, which takes into account a U.S. inflation rate of 1.9%. The real selling price of ammonia in the U.S. was taken to be \$355 per short metric ton[58] adjusted by the January 2019 Commodity Price Index value. Other assumptions include a catalyst life of half a year and the supply of electricity from the medium voltage grid distribution network in the U.S.

For nitrogen generation and the electrochemical cell, equipment was sized and cost using Aspen Plus™ Economic Analyzer, similar processes in the literature and heuristics[59]. The literature values were adjusted for change in capacity[60] using the following equation:

$$C_b = C_a \left(\frac{A_b}{A_a} \right)^n \quad [5]$$

where C_b is the required cost, C_a is the base cost, A_b is the required attribute, A_a is the base attribute and n is the cost exponent. Attribute in equation [5] is related to the capacity of the piece of equipment. Values are also adjusted for time[60] as follows:

$$C_b = C_a \frac{I_b}{I_a} \quad [6]$$

where I_b is the required index, I_a is the base index. Index in equation [6] refers to the Chemical Engineering Plant Cost Index (CEPCI). The January 2019 CEPCI value was used.

For hydrogen production, the current H2A future central analysis models[61] provided by the U.S. DOE were adapted and parameters updated for assumptions, the effect of time and capacity.

Economics for all membrane systems include replacement costs. It is assumed membranes are replaced every five to ten years to account for membrane aging effects.

For the electrochemical cell for ammonia synthesis, a basic two-compartment configuration with an electrolyte membrane for passage of the hydrogen ions from the anode to the cathode. The selected configuration is the direct reduction of nitrogen at the cathode in the presence of the H^+ ions generated from water electrolysis. The case of a direct water feed to the electrochemical cell as another possible route was not studied as it places additional constraints on catalytic materials [51] selection. It is doubtful that the process conditions and electro-catalysis can be simultaneously optimized for both water electrolysis and ammonia synthesis. Aspen Plus™ Economic Analyzer was used for sizing of the electrochemical reactor and catalyst as well as membrane materials were cost at current bulk prices.

Results and Discussion

Capital Investment and Manufacturing Costs

Nitrogen Source Selection

The diatomic nitrogen used in ammonia synthesis is generated on an industrial scale by three major methods: pressure swing adsorption (PSA), membrane separation (MS) and by cryogenic distillation column (CDC). The PSA method uses compressed air (6-15 barg) and is a repetition process of adsorption and desorption. It commonly uses two adsorption towers packed with carbon molecular sieves (pore diameter 3-5 Å) adsorbent to allow adsorption of oxygen molecules (3.46 Å) to the sieve pores and nitrogen (3.64 Å) gas removal in the tower exhaust to storage. As the adsorbent becomes saturated, valves in the system are adjusted to redirect the feed to a second column. The adsorbent in the first column is regenerated at reduced pressure and desorbed oxygen gas is captured or vented to atmosphere. The membrane separation system on the other hand, uses a hollow-fiber microporous membrane[62] to carry out selective permeation of oxygen and rejection of nitrogen dictated by permeability and selectivity. Lastly, an ambient air feed is used in cryogenic distillation column to separate low-boiling components. The air is separated into gaseous oxygen and nitrogen by distillation. Purity in these methods can be increased by adjusting residence time. PSA compared to membrane systems is more sensitive to the presence of moisture in air, which leads to reduced capacity and permanent damage of the sieves. However, at higher purities of 99.999%, PSA is considered more efficient than membrane systems which give purities up to 99.9%. Additionally, it should be noted membrane systems may need the addition of a hydrogen bleed and downstream catalyst to oxidize the residual free oxygen to water vapor. The cost for the balance of plant (BoP) consisting of instrumentation, piping, tanks and air pre-purification is taken to be 55% of the total capital investment for nitrogen generation. Air compressors of the centrifugal type operating at 0.65 MPa driven by electric motor using approximately 500 kW was selected for cost estimation. The BoP and air

compressor were considered common with equivalent cost for all three nitrogen generation methods. The capital costs for the three methods are shown in Figure 7.

Again, the main pieces of equipment for nitrogen generation were cost using Aspen Plus™ Economic Analyzer and heuristics[59]. The adsorption towers were cost as fixed bed cylindrical towers with regeneration auxiliary equipment with controls using a volumetric air flow rate of approximately 81 dm³/s. The membrane was cost as a flat hollow fiber setup including auxiliaries to achieve 98% mole purity in the retentate stream. The distillation columns were simulated as 0.6 m diameter towers containing 316 stainless steel sieve trays. From figure 7, the CDC systems have a high total capital cost when compared to PSA and membrane systems. Although they can cost upwards of \$15 MM, they can accommodate high production rates, that is, greater than a 5000 metric ton/day air feed.

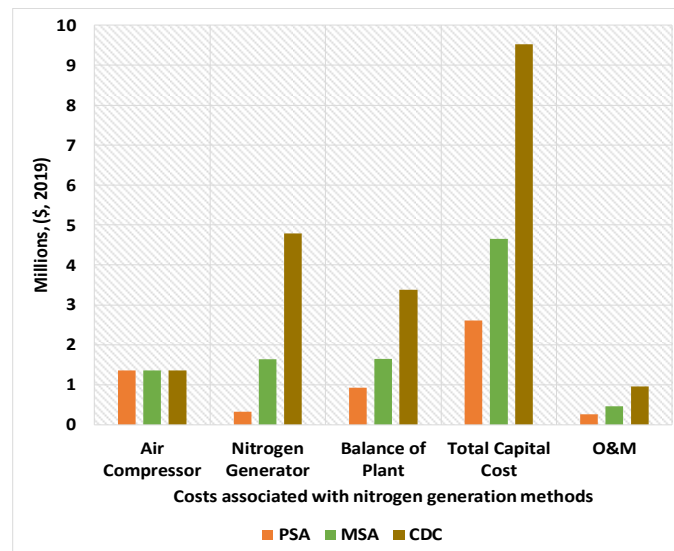


Figure 7: Capital cost analysis of nitrogen generation by pressure swing adsorption (PSA), membrane separation (MS) and cryogenic distillation column (CDC). Operation and maintenance (O&M) costs for each method are also shown.

Hydrogen Source Selection

Hydrogen can be obtained by processing of waste (industrial, food, animal, forestry), coal, natural gas, water, biomass and refinery products including ethylene, petroleum coke and gasoline. The processing of these feedstock materials can take place by steam methane reforming (SMR), solid oxide (SO) and polymer electrolyte membrane (PEM) electrolysis, photo-electrochemical, solar thermochemical and gasification methods. The economics for hydrogen production was carried out for steam methane reforming, the main method for converting natural gas to H₂, and low temperature electrolysis which is powered by renewable energy sources. The balance of plant (BoP) for plants utilizing these technologies include process control equipment, pumps, blowers, power electronics and sensors. Figure 8 shows the capital costs for these chosen methods. It can be seen that the total capital costs amongst the different methods is largest for SMR and found to be upwards of \$70 million (MM) and \$80 MM without and with CO₂ capture respectively. The capital cost of SMR is high as it uses reactors including the reformer. Electrolysis technologies were found to be up to 70% of the SMR total capital cost. The capital cost of SMR is high as it uses a reformer which accounts just over 60% of the SMR total capital cost. Balance of plant which includes power electronics and conditioning of the gas, is lower

overall for electrolysis technologies and is projected to decrease as operating temperatures are

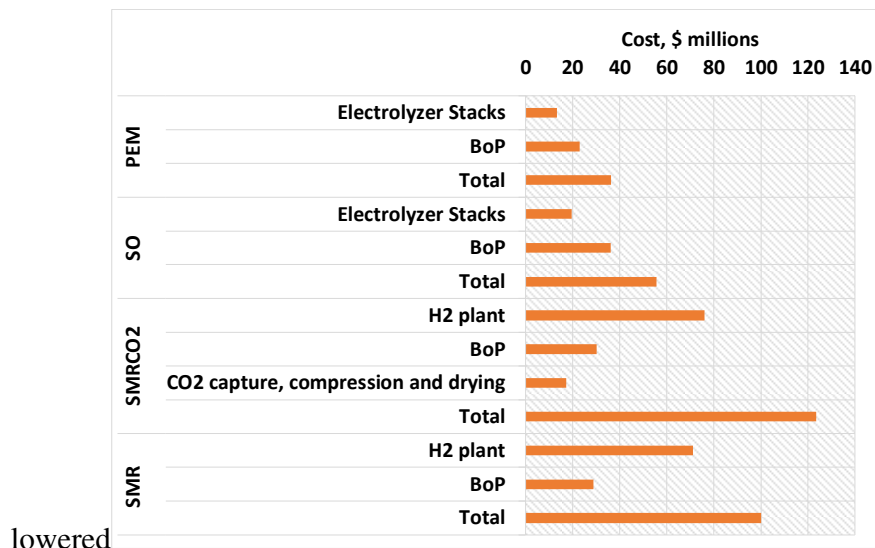


Figure 8: Capital cost analysis for hydrogen production by various methods including steam methane reforming (SMR), SMR with carbon dioxide (SMR_{CO2}) capture, solid oxide (SO) electrolysis and polymer electrolyte membrane (PEM) electrolysis

PEM electrolysis uses expensive catalysts and is a complex system to manage with electrochemical cell processes. Although, PEM electrolysis has a higher capital cost than SOE due to technological maturity, it is projected the capital cost for solid oxide electrolysis will increase as materials are developed for thermal management.[63] Additionally, the total (fixed and variable) operating costs for electrolysis and SMR technologies without CO₂ capture were found to be up to \$6.66 and \$11.95c per kg H₂ respectively with capital cost included. The estimated electricity requirements for the various hydrogen production technologies is shown in Figure 9. The energy consumption for the hydrogen production methods were estimated using the H2A models. [61] The industrial electricity demand is higher for PEM and SOE upwards of

35000 kW for a daily production rate of approximately 16,000 kg H₂/day compared to SMR which is thermal energy based and consumes almost 90% less electricity.

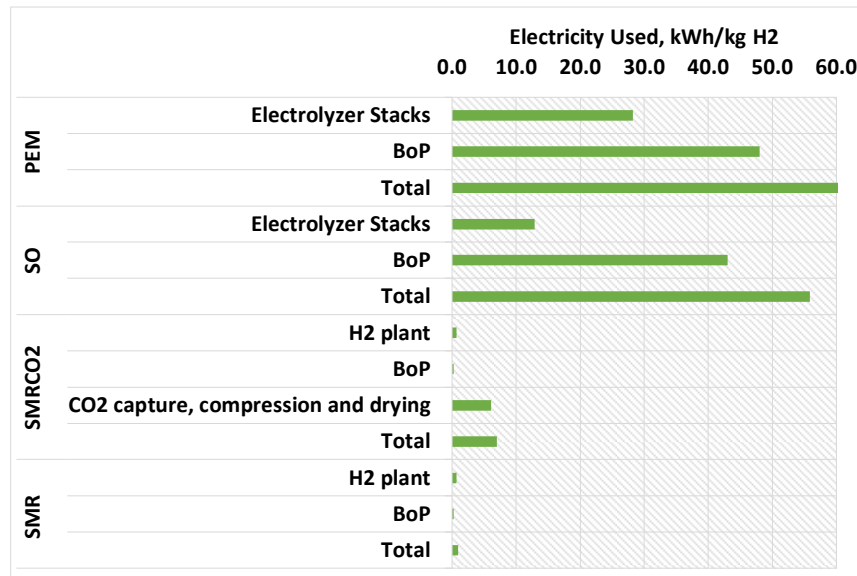


Figure 9: Electricity usage analysis for various hydrogen production methods.

In electrolysis, it is known electrolyzers consume electrical current to split the water into hydrogen and oxygen. As the efficiency of the low temperature electrolysis technologies improve, the energy consumption should also be reduced to produce energy savings.

Electrochemical Ammonia Synthesis

Ammonia is produced commercially via the H-B process but uses operating conditions of special concern for the gaseous reactions. The pressure, $P > 10$ bar, gives favorable equilibrium conversion of the gaseous reactants but requires thick-walled construction for equipment including reactors, piping and compressors other process equipment. The use of special materials of construction also holds true for the high temperature, $T \geq 250$ °C, as it increases reaction rates and breaks the strong nitrogen triple bond.

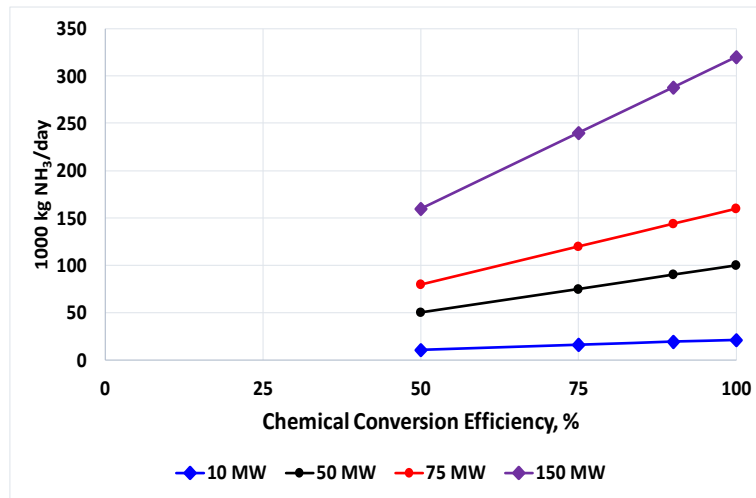


Figure 10: Relationship between overall chemical conversion (nitrogen to ammonia) efficiency and ammonia daily production rate

H-B currently does not work well on a large-scale with intermittent energy inputs and on a small-scale of less than 100 MW, it is neither cost effective nor efficient. The electrochemical synthesis of ammonia can take place at low temperatures, $T \leq 200$ °C, and near ambient pressure with increased efficiency toward economies of scale. Figure 10 illustrates this point simply where the daily ammonia production rate goes up with higher overall chemical conversion efficiency. Also, the specific energy decreases as the production rate increases and supports the notion that the energy efficiency of the plant depends on production level.

Figure 11 shows the relationship between number of electrochemical cell modules and current density as plant size varies.

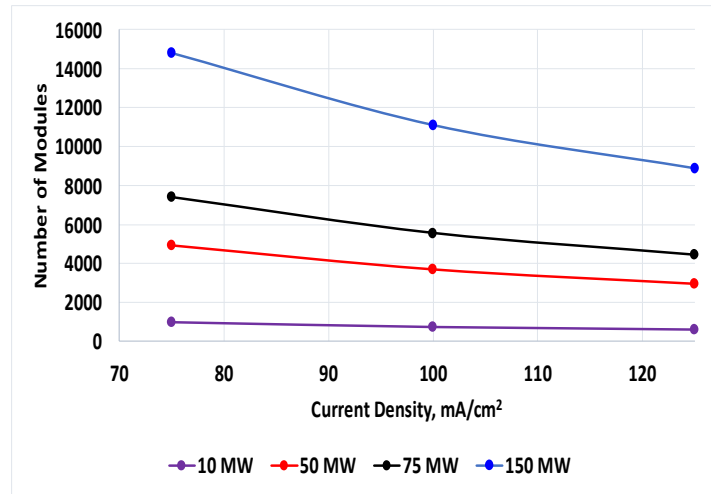


Figure 11: Relationship between current density and number of modules for electrochemical ammonia synthesis

The electrochemical cells are brought together in a compact design consisting of modules containing electrodes connected in parallel and modules connected in series. It can be seen that the number of modules decreases with current density with higher values obtained for a 150 MW plant. Current density values are still low with the highest reported value at 3 mA/cm² at 100% current efficiency when compared to the ARPA-E REFUEL target. [64]

The types of solid or composite proton electrolyte membranes can range from perovskites and perfluorosulfonic to polysulfone. Two of the highest reported ammonia production rates using nitrogen and hydrogen gaseous reactants for temperatures, $T < 100$ °C, were for perfluorosulfonic and sulfonated polysulfone (SPSF) electrolyte membranes with values equal to 1.05×10^{-8} and 1.03×10^{-8} mol s⁻¹cm⁻² respectively.[65] These results were both obtained at 80 °C and +2.5 V. Perfluorosulfonic membranes are stable chemically and thermally but are expensive, \$600-1000/m². Electrode materials can be metal oxides, metal nitrides, precious

metals, ceramics and composite metal. It should be noted that the development of catalysts for the electrochemical nitrogen reduction reaction (NRR) is an important consideration to bring about low temperature operation of the electrochemical cell and better Faradaic efficiency.

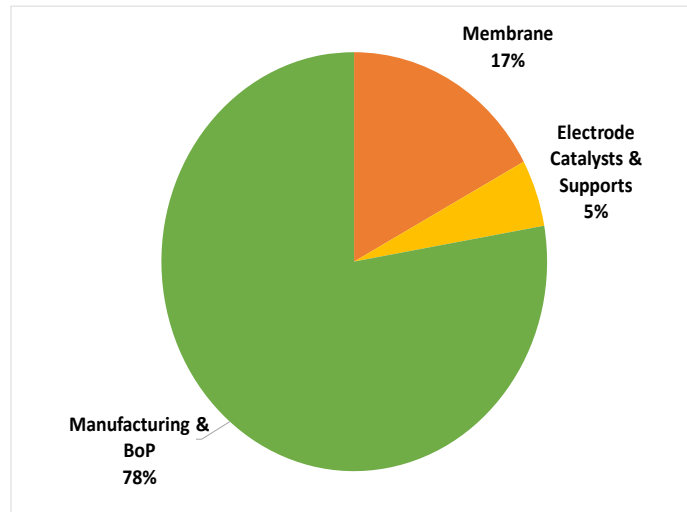


Figure 12: Capital cost analysis breakdown for major components of the electrochemical device. The total capital cost is \$2.6M.

Figure 12 shows the electrochemical device cost breakdown based on high cost scenario. The high cost scenario uses perfluorosulfonic membrane, noble metal-based electro-catalysts for both anode and cathode and metal paste current collectors. The balance of plant includes piping and gas transport to the electrochemical cell. Although, the electrochemical cell is based on the ARPA-E REFUEL target[64], the model can be adjusted as more data is obtained and this target is used as a starting point assumption for economic viability.

Profitability and Sensitivity Analysis

Table 2 shows the variation in plant type for electrochemical ammonia synthesis in comparison with H-B technology. H-B plant economics includes costs and energy consumption for hydrogen buffer storage, compression and recirculation. The electrochemical route for ammonia has the lowest energy consumption for most combined system types. The lowest total cost is anticipated for electrochemical synthesis combined with hydrogen by water electrolysis and cryogenic air separation for nitrogen based on future technology improvements. For the profitability of the project, cumulative after-tax cash flow diagrams demonstrating several ammonia synthesis scenarios is shown in Figure 13.

Table 2: Breakdown of costs and energy for the electrochemical reactor (ER) and Haber-Bosch (H-B) with different hydrogen source integrations steam methane reforming (SMR), SMR with carbon dioxide (SMR_{CO₂}) capture, solid oxide (SO) electrolysis and polymer electrolyte membrane (PEM) electrolysis as well as nitrogen generation by air separation unit (ASU)

System Type	Total Energy Consumption, kWh/kg NH ₃	Total Electricity Cost, \$/ 1000 kg NH ₃	Total Capital Cost (CAPEX), \$/ 1000 kg NH ₃	Total Operating Costs (OPEX), \$/ 1000 kg NH ₃	Ammonia Cost, \$/ 1000 kg NH ₃
ER + SMR _{CO₂} +ASU	26.3	\$263	\$880	\$294	\$1,437
ER+SMR+ASU	25.2	\$252	\$797	\$263	\$1,312
ER+SO+ASU	28.7	\$287	\$528	\$154	\$969
ER+PEM+ASU	32.4	\$324	\$459	\$168	\$951
H-B +PEM+ ASU	29.7	\$297	\$522	\$157	\$975

These diagrams were constructed using an electricity price of \$0.010 c/kWh. The discounted cash flows increase steadily from year 2 when revenue is generated to year 20 when operation ends and additional cash flows from working capital, salvage value and cost of land are

recovered. It is observed that SMR technologies, when combined with either electrochemical ammonia synthesis or H-B process, requires higher capital investment spread over the first two years when compared to the electrolysis technologies. Additionally, the steeper gradients observed with the electrolysis technologies is attributed to the smaller capital investment. The cash flow diagrams yield positive net present values across the various scenarios for an 8% discounted cash flow rate of return or DCFROR.

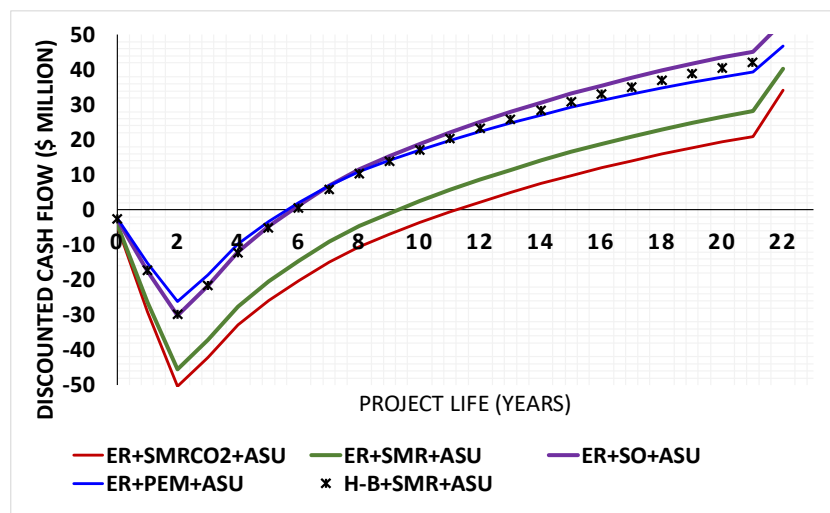


Figure 13- Cumulative cash flows for discounted after-tax scenario for the electrochemical reactor (ER) with different hydrogen production methods including SMR, SMR_{CO2} capture, SO and PEM as well as nitrogen generation by ASU in comparison with small scale H-B.

Both electrolysis technologies when integrated with the electrochemical production can be competitive with H-B to potentially yield the higher net present value of \$40 MM across scenarios with discounted payback period (DPBP) between 4 and 6 years. H-B in combination with SMR hydrogen generation yields a 26% lower NPV value and longer DPBP upwards of 7 years. It was generally found, DPBP was higher when ER and H-B were combined with SMR

hydrogen production methods. Sensitivity studies were carried out for one of the most influencing model parameters, price of electricity, as shown in Figures 14a and 14b.

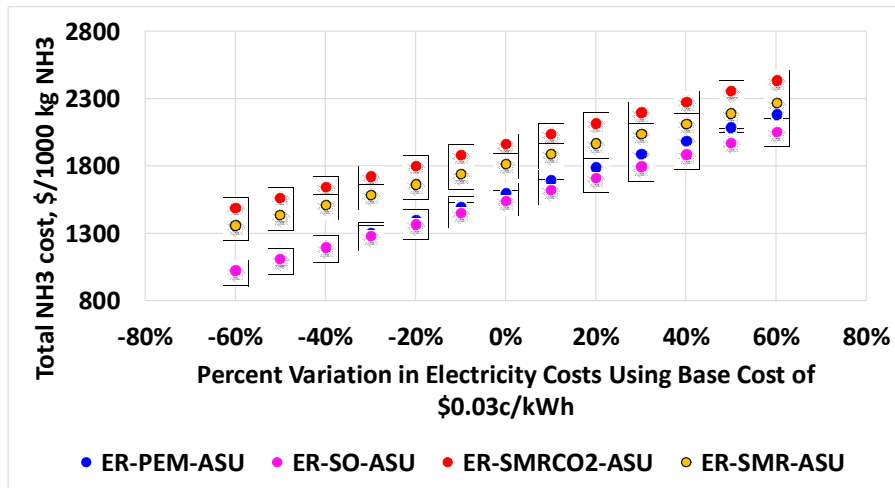


Figure 14a: Sensitivity analysis showing electricity price variation and the effect on total cost of ammonia production by electrochemical reactor which combines different hydrogen source integrations including SMR, SMR_{CO2} capture, SO and PEM as well as nitrogen generation by ASU in comparison with small scale H-B.

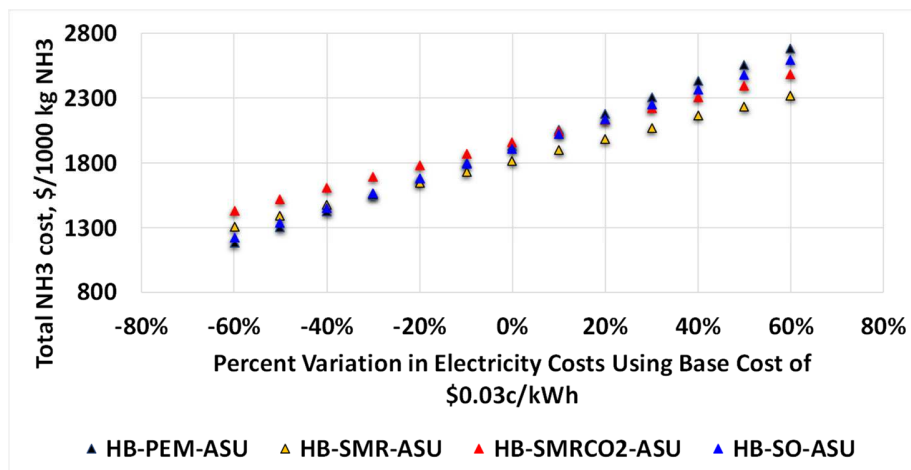


Figure 14b: Sensitivity analysis showing electricity price variation and the effect on total cost of ammonia production by small scale H-B which combines different hydrogen integrations including SMR, SMR_{CO2} capture, SO and PEM as well as nitrogen generation by ASU in comparison with small scale H-B.

The electrochemical synthesis of ammonia is attractive and can potentially be more competitive with small-scale H-B if electricity prices are equal to or less than \$0.01 c/kWh.

Cradle to Gate Life Cycle Assessment for Ammonia by Haber-Bosch and Electrochemical Methods The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) 2018 Model by Argonne National Laboratory [66] developed in 1994 was used to assess the environmental impact of the ammonia production process by Haber –Bosch and electrochemical methods. The GREET model includes well-to-product energy and GHG emissions analysis for over 100 fuel pathways. It includes the H2A models for hydrogen which were used directly from the database. Mass and energy flows for the LCA model were obtained from the techno-economic assessment carried out earlier in this paper. A process based LCA governed by ISO for the end-product ammonia was carried out. Electricity production was assumed to be a generation mix of primarily 63% fossil fuels, 20% nuclear and 17% renewable energy resources.[67]. The GREET's database for ammonia production was adapted for electrochemical ammonia via the electricity consumption. Figure 15 shows the system, where solid arrows indicate material and energy flows. The dashed lines represent the process boundaries and is one of the first steps of life cycle assessment (LCA). Life cycle stages from well to liquid ammonia product for the LCA are shown within the process boundaries. The detailed steps associated with the production and distribution of natural gas, electricity and other utilities were obtained from the GREET database.

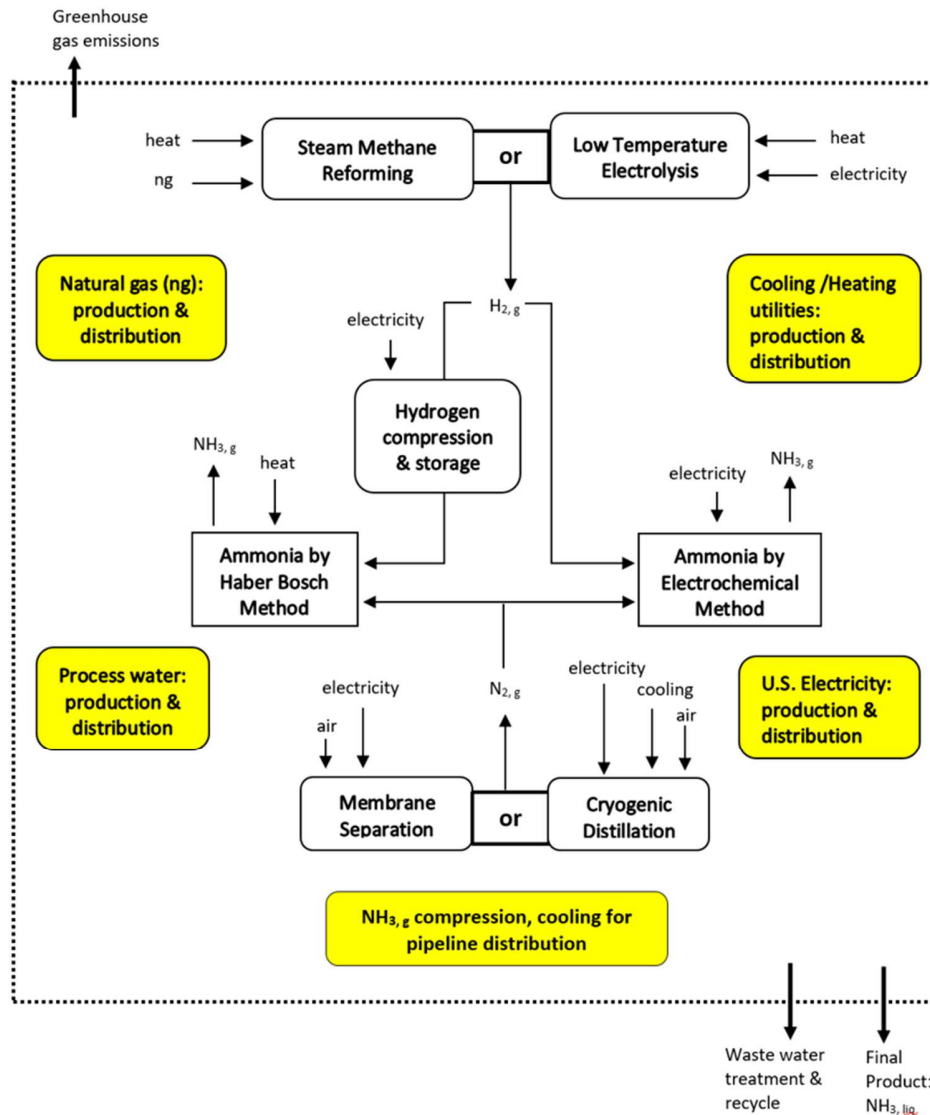


Figure 15. System definition for the life cycle assessment showing inventory of main flows from well to product. Flows for the raw material and final product processing (in yellow rectangles) are not shown.

The results of the LCA include air emissions and resource consumption. The functional unit was selected on a per 1000 kg NH_3 basis averaged over a one-year production rate. The two major ammonia production methods for comparison in this LCA are electrochemical and traditional

Haber-Bosch. Figure 16 shows CO₂ is emitted in the largest quantity for hydrogen production during the raw material processing stage compared to nitrogen generation which is lower by two orders of magnitude.

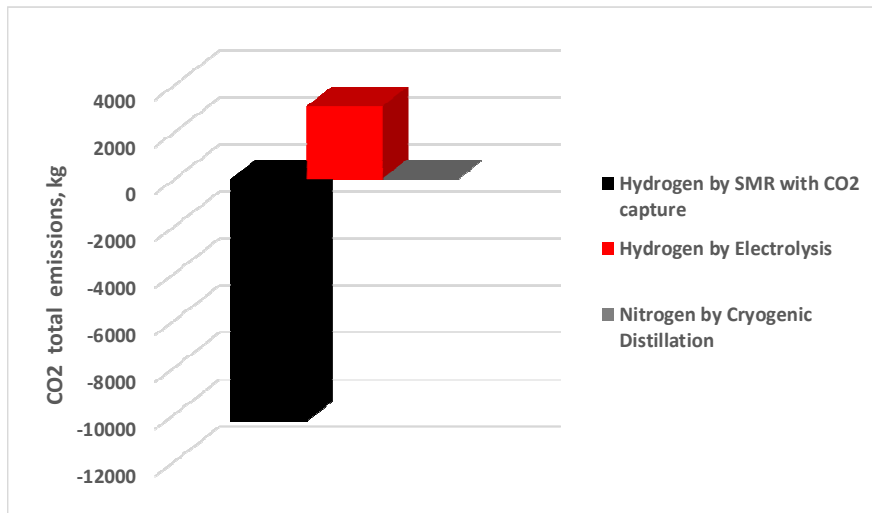


Figure 16. CO₂ emissions for hydrogen production and nitrogen generation.

Hydrogen production by water electrolysis produces 70% less CO₂ emissions when compared to SMR without carbon capture and storage (CCS). For the SMR process to be used as a carbon neutral source of hydrogen in ammonia production, CCS is needed. Carbon capture technologies include pre-combustion, post-combustion and oxy-combustion all of which come with the challenge of transporting and then storing CO₂. Figure 17 is a well to ammonia product comparison between the Haber-Bosch and electrochemical methods. It emphasizes the hydrogen production as the largest CO₂ emissions source. Ammonia by electrochemical method powered by renewable electricity throughout will bring us closer to having a carbon neutral process. It is understood carbon emissions will be present during the manufacturing of renewable technologies.

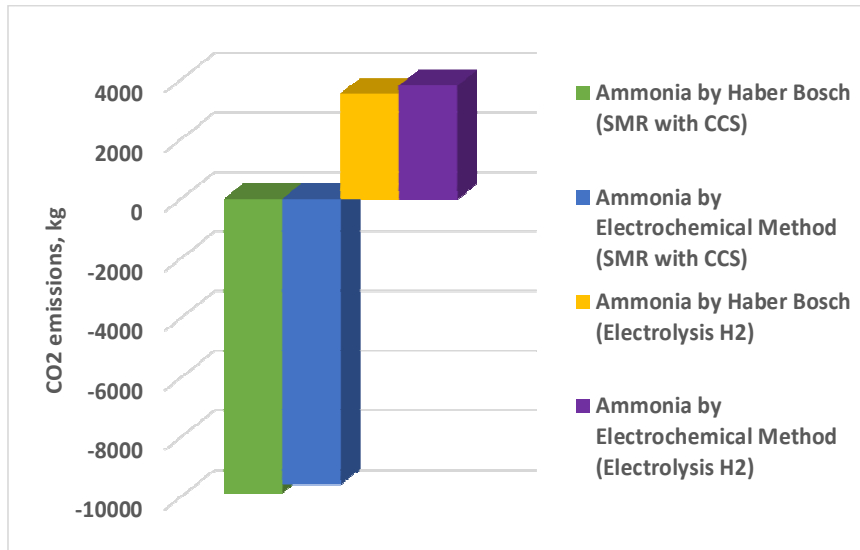


Figure 17. Variation in CO₂ emissions for well to product ammonia processes

Emissions by other greenhouse gases (excluding carbon dioxide because of its magnitude) and air pollutants from the ammonia production processes are shown in Figure 18. Volatile organic compounds (VOCs) is shown as the second major emissions source largely (>99%) produced by the Haber-Bosch process followed by methane (CH₄), nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), black carbon (BC) and primary organic carbon(POC), particulate matter (PM_{2.5} and PM₁₀), and nitrous oxides (N₂O).

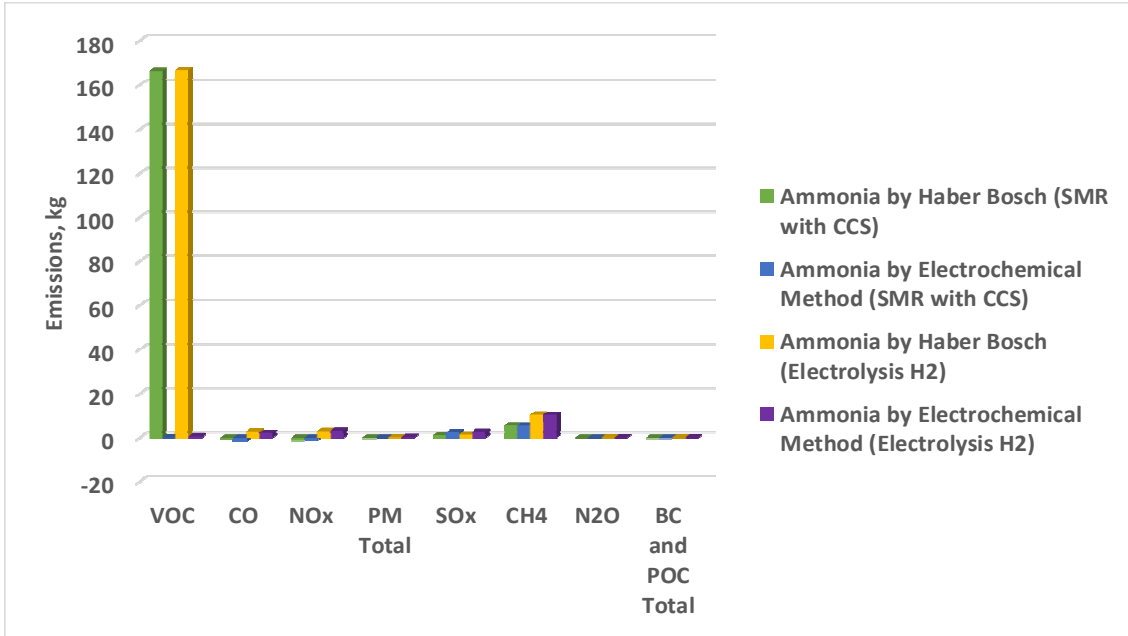


Figure 18. Emission contributions for well to product ammonia processes

Figure 19 shows the consumption of renewable and non-renewable energy resources

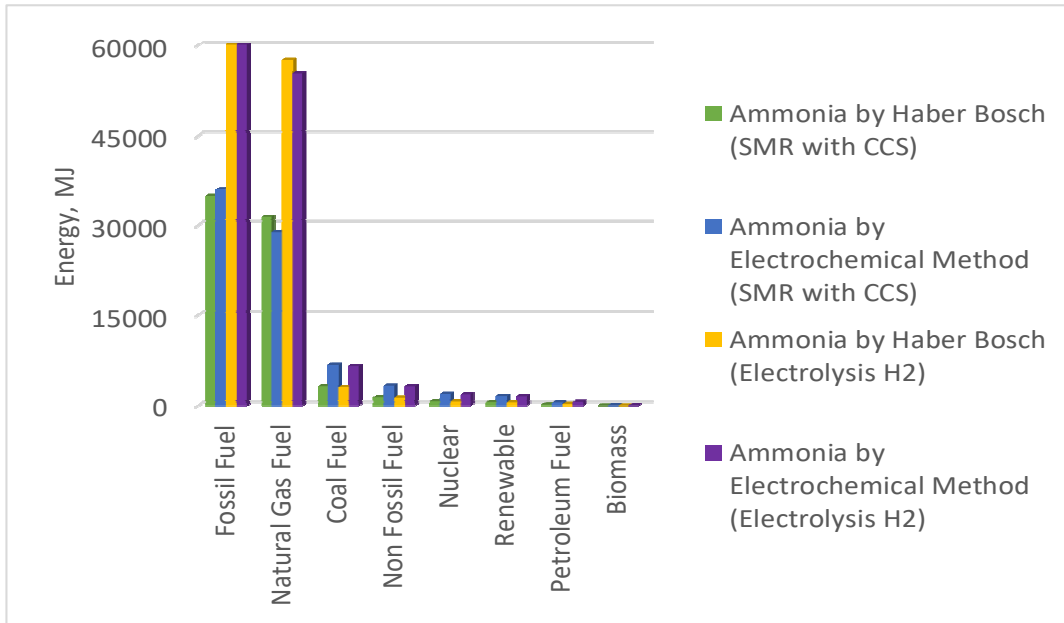


Figure 19. Resource consumption for well to product ammonia processes

which is a major component of the LCA. Fossil and natural gas fuels are consumed in the largest amounts across all methods accounting for about 90% of the total resources. This primarily arises from the natural gas processing and distribution as well as conversion to hydrogen and electricity. Once again, the large intake of energy resources can be greatly reduced by using renewable electricity. Hydrogen production by SMR without CCS will result in a higher resource consumption, upwards of 75% of the energy value indicated for electrolysis. From the results, for every metric ton of ammonia as much as 17 MWh of energy can be consumed. This value is within the range of uncertainty for the estimated energy consumption in the techno-economic model discussed previously.

Water consumption across the ammonia production methods is shown in Figure 20.

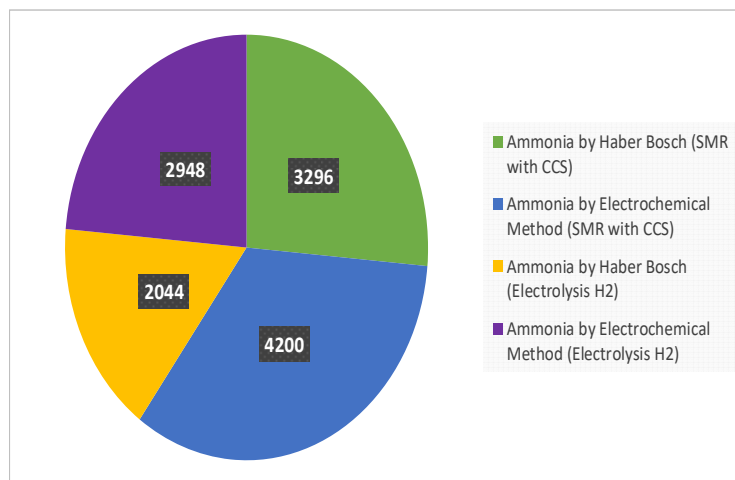


Figure 20. Water consumption (U.S. gallon) for well to product ammonia processes

The pie chart divides water usage in U.S. gallon for each ammonia process. Water is primarily used in hydrogen production and as a process utility. The majority of the water is consumed in the hydrogen production stage across all methods. It is observed that hydrogen production by

SMR with CCS uses a greater quantity of water due to natural gas extraction and fuel production compared to electrolysis. When analyzing methods, water usage is higher for ammonia produced electrochemically than by Haber Bosch. This is attributed to the electricity directly used in the electrochemical process.

Conclusion

A full techno-economic model for the electrochemical synthesis of ammonia was developed for a base capacity of approximately 140 metric ton/day ammonia. Different process couplings for hydrogen production and nitrogen generation with the electrochemical cell were assessed for their economic impact. All the couplings are economically attractive but is highly dependent on electricity price. The hydrogen by water electrolysis pathways proved potentially as viable as the SMR pathways. In this analysis, using a desired electricity price of \$0.01 c/kWh for the electrochemical and hydrogen by water electrolysis integrations, the yearly operating costs were found to be upwards of \$30 MM and DCFROR was around 34% to break even at an NPV value of zero. Integrated electrochemical ammonia systems with renewable intermittent sources has linear scalability advantages and offer potential opportunities for the development of truly sustainable liquid ammonia. However, it should be noted that the ARPA-E REFUEL target of $9.3 \times 10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$ for the ammonia rate with 90% Faradaic efficiency and current density of 300 mA cm^{-2} has not been met. Electrochemical-based research trends continue to emerge across different groups working on mild operating conditions with present progress yielding 56% Faradaic efficiency[45], $1.03 \times 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$ for the ammonia formation rate[65] and 20 mA cm^{-2} for the current density.[48] Future work should continue to focus on the understanding and development of low temperature conditions, reaction kinetics, electrolyte development and

tuning of the electro-catalyst materials to attain better Faradaic efficiencies and higher ammonia conversion rates at improved current densities. Furthermore, the study highlights the environmental feats from energy resource savings to near zero emissions that can be achieved by powering electrochemical ammonia and hydrogen production with renewable electricity. The following concluding remarks are drawn for this study

- Integrated electrochemical ammonia systems with renewable intermittent sources has linear scalability advantages
- Energy consumption of at least 17 MWh per metric ton for electrochemical ammonia
- Number of electrochemical modules decreases with current density
- Specific energy decreases as the production rate increases

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