



Team Senior Citizens
Ghausi Hall, Davis, CA 95616

June 9, 2023

Dr. Matthew Ellis, Project Manager
Modular Engineering
1 Shields Avenue
Davis, CA 95616

Dr. Matthew Ellis,

Enclosed you will find our "Parallel Modular Manufacturing of Green Anhydrous Ammonia" report, which was requested on April 3, 2023.

Modular Engineering's strides towards small-scale chemical manufacturing have presented new opportunities to supply the U.S. corn belt with a reliably cheaper source for anhydrous ammonia. Our goal was to use the principles of modular manufacturing to design a fully-contained, small-scale ammonia synthesis plant that will be used in Minnesota. The plant will use NEL alkaline electrolyzers and molecular membrane separation to supply the hydrogen and nitrogen for the ammonia reaction, respectively. The reaction will take place in a packed bed reactor with Ru/C catalyst held near 100 bar and 350°C, and ammonia will be collected via flash separation. The plant will be capable of supplying 99.8% anhydrous ammonia by weight at a rate of 51 metric tons per day while having zero carbon footprint.

An economic evaluation of the modular ammonia plant was performed based on a plant operational timeline of 20 years, utilizing net present value (NPV), modified internal rate of return (MIRR), discounted cash flow rate of return (DCFRROR), and before tax return on investment (BTROI) as profitability metrics. Based on a MACRS schedule of 10 years, the NPV, MIRR, DCFRROR, and BITROI were determined to be \$17.39 million, 15.00%, 15.60%, and 24.99%, respectively, indicating favorable economic forecast of the plant.

Thank you for giving Team Senior Citizens the opportunity to design a process using modern novel technology. If any part of this report is unclear, please do not hesitate to contact us.

Sincerely,

Joseph Azizpor

Joseph Azizpor
Reliability Engineer

Garlen Chan

Garlen Chan
Engineer of Process

Max Schenck

Max Schenck
Chemical Engineer

Frank Vilimek

Frank Vilimek
Process Control
Engineer

Encl. Engineering Report

Department of Chemical Engineering
University of California, Davis

Emission-Free Local Ammonia Production Plant Design

Joseph Azizpor, Garlen Chan, Max Schenk, Frank Vilimek
Prepared under Professor Matthew Ellis
ECH 158C Spring Quarter 2023
June 9, 2023

Abstract

A small-scale modular ammonia plant design is proposed for the purpose of supplying states in the US corn belt with cheap and available anhydrous ammonia at a rate of 50 metric tons per day. The plant will be located primarily in Minnesota, and as such it is designed with Minnesota state regulations, permits, and natural resources in mind. Processing equipment were sized using design heuristics and were implemented in an Aspen Plus V12 simulation for more accurate optimization. The proposed ammonia plant will use molecular membrane separation to source nitrogen, NEL A3880 electrolyzers to source hydrogen, and a modified Haber-Bosch process that utilizes Ru/C catalysts for the ammonia reaction. The Ru/C catalysts have been found to provide similar conversions to the traditional iron-based catalysts, yet operate at reduced temperatures and pressures of 450°C and 100 bar compared to the 600°C and 200 bar operation of traditional Haber-Bosch. These reduced conditions provide a more energy-efficient and safer design compared to Haber-Bosch. The process will require a total of 42.6 metric tons of nitrogen per day and 9.21 metric tons of hydrogen per day to produce 51 metric tons of ammonia per day. Based on the sizes of the equipment in the Aspen simulation, a preliminary economic analysis was performed to determine the viability of the plant. The profitability of the plant was evaluated by the NPV, BTROI, DCFROR, and MIRR of the plant at the end of the proposed 20-year project lifetime. The plant was found to be profitable: an ammonia price of \$1,100 per ton and a 10-year MACRS schedule provided the best NPV value of 17.39 million, which corresponded with a BTROI of 24.99%, a DCFROR of 15.60% and an MIRR of 15.00%. The process achieves practically entirely green operation to produce 51 tons of 99.8 wt% ammonia per day while projecting an economically viable forecast, therefore it is recommended to proceed with the proposed design.

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Introduction

Background Information

The synthesis of ammonia is one of the most important processes of all time, supplying ammonia as fertilizer to grow crops that feed half of the world's population. Also known as the Haber-Bosch process, ammonia is generated through a reaction between hydrogen and nitrogen at a 3:1 stoichiometric ratio, as illustrated by equation 1.



Although this process is critical for sustaining current human demands, it contributes to roughly 1-3% of global energy consumption, 5% of global natural gas consumption, and around 3% of greenhouse gas emissions annually^[1]. This poses serious risks to the environment and could significantly accelerate climate change. Moreover, the Haber-Bosch process currently operates at temperatures and pressures of around 400-600°C and 200-400 bar, posing serious safety risks to operators as well^[1]. To combat these environmental and safety concerns, Modular Engineering tasked Team Senior Citizens to develop a modular ammonia production process with environmentally-friendly and safer solutions in mind, capable of being operated by farmers near the US corn belt and reducing transportation costs with ammonia production at point-of-use locations.

Design Considerations

Current alternative methods of ammonia production being researched include non-thermal plasma (NTP) catalysis, as well as alternative catalysts beyond the traditional iron-based catalysts of the Haber-Bosch process. NTP catalysis is the process in which non thermal plasmas (i.e. microwave plasma, etc.) are used to increase the efficiency of catalysts through the ionization of gaseous compounds during the ammonia synthesis reaction. Although NTP catalysis shows promising improvements in operating conditions relative to the traditional ammonia production process, the immediate decomposition of ammonia and subsequently low conversion rates make this process less desirable^[1]. However, using a ruthenium-on-carbon (Ru/C) catalyst with the traditional ammonia synthesis loop provided promising results, as it showed iterative improvement to conversions of ammonia accompanied with lower operating temperatures and pressures^[2].

For the upstream production of hydrogen, two methods are considered: steam methane reforming (SMR) augmented with a water-gas shift (WGS) reaction, and electrolysis. SMR is the process in which methane is reacted with high-temperature steam (700-1,000°C) to form hydrogen along with carbon monoxide, and WGS is the process in which carbon monoxide and steam is reacted

to form carbon dioxide and hydrogen^[3]. Although both processes have been well established in industry for large scale processes, they both require burning fossil fuels to attain their optimal operating conditions. Electrolysis, however, is the process in which hydrogen is produced via an electric current passed through water, and is the most promising hydrogen production process as it does not require burning fossil fuels. Due to its inherently low carbon footprint, electrolysis was the recommended hydrogen production process for the modular ammonia production plant.

As for the upstream production process of nitrogen, three methods were also considered: cryogenic distillation (CD), pressure swing adsorption (PSA), and molecular membrane separation (MMS). CD is the process in which air is liquefied through pressurization with inter-stage cooling, then the nitrogen components are separated from oxygen and various contaminants via distillation and molecular sieves. Although it is the oldest and most widely-used nitrogen production method, dating back to the 1890s and making up 65-70% of total nitrogen production, it is only economically viable for large-scale, stick-built production plants^[4]. PSA is also a well-established process for high-purity nitrogen production, in which atmospheric oxygen is adsorbed to a pressurized adsorption column and allows nitrogen to pass through via carbon molecular sieves. Although PSA is economically viable for the target purity and flow rate, the heavier equipment makes it less suitable for modularity^[5]. On the other hand, MMS is the process in which air is compressed through various membrane modules, where oxygen is separated from nitrogen and passes through the membrane as a permeate via selective gas permeation, leaving the nitrogen to be collected. Operating at a purity of 99.9% with high flow rates of nitrogen, the energy duties for CD and PSA were found to be as high as 0.7 kWh/Nm³ N₂ and 0.46 kWh/Nm³ N₂ respectively, while MMS was found to operate as low as 0.07 kWh/Nm³ N₂ with more suitable flow rates^[6]. As mentioned previously, CD and PSA utilize much heavier equipment than MMS, as distillation columns and adsorption beds tend to be heavier and cumbersome versus lightweight hollow polymeric membranes^[7]. This lightweight design not only makes MMS more suitable for modular process designs, but it can also help lower transportation duties for module delivery and replacement at point-of-use locations. Due to lower energy duties and lightweight design, MMS was recommended for this modular ammonia production process.

Sourcing Hydrogen Through Electrolyzers

Hydrogen production is traditionally made through the steam methane reaction where 48% of all hydrogen production is currently produced by this method^[8]. The choice to produce hydrogen gas from electrolysis was motivated by the fact that it produces virtually no carbon emissions and can be powered through renewable means. Hydrogen gas production during ammonia synthesis is the largest source for carbon emissions^[9]. An alkaline electrolyzer was the choice for electrolysis due being able to achieve high throughputs up to 20,000 normal meter cubed per hour (Nm³) and it has a high stability compared to alternative methods^[10]. Polymer Electrolyte

Membrane (PEM) electrolysis did not meet the required amounts of hydrogen gas to be produced and high operating costs from catalytic deactivation^[11]. Solid Oxidation electrolysis was another option, however they require high temperatures around 500-900°C that can only be achieved with a fossil fuel powered furnace, or an extremely high-cost electrical system^[12]. Alkaline electrolyzers work by having an electrolyte in a solution of water, usually potassium hydroxide, and a current is run through the solution to electrically split the bonds between oxygen and hydrogen. The NEL A3880 Electrolyzer is a maximum power of 17.6 MW alkaline electrolyzer and meets the requirements and it is transportable via truck to fit the modular method of synthesis. The electrolyzer itself is capable of producing hydrogen gas at 99.99% purity. This is attractive because having as little oxygen gas in the downstream process is beneficial to avoid any oxidation on the catalyst, and the production of noxious reagents like nitrous oxide will be minimized. The NEL A3880 produces up to 5,180 kg/day of hydrogen gas on its lowest setting and over 8,000 kg/day on its max operation setting. The maximum setting does not meet the required daily amounts so two electrolyzers on their lowest setting would suffice.

Principles of Molecular Membrane Separation for Sourcing Nitrogen

The production of ammonia requires an inlet nitrogen purity of 99.9% to prevent catalyst poisoning and oxidation of materials, and high-purity nitrogen can be sourced from MMS. As previously stated, not only are conventional MMS systems lower in energy duty when compared to CD and PSA systems, but the equipment weight of MMS systems is much lower compared to distillation columns and adsorption beds for CD and PSA, making it more suitable for modular design for small-scale production at point-of-use locations.

As seen in figure 1, MMS is based on selective gas permeation, in which a gas mixture is passed through a tubular membrane module and faster gasses are permeated out of the mixture, leaving the desired, slower gas to flow through the tube. For selective gas permeation, the primary driving force for separation is assumed to be a pressure difference.

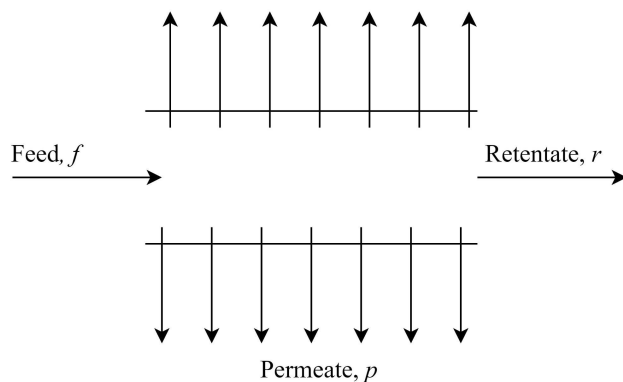


Figure 1. Simplified schematic diagram of selective gas permeation in MMS design.

For the nitrogen production process, air is fed into the MMS system and the permeate and retentate will be oxygen-rich and nitrogen-rich streams, respectively. Since conventional filtration methods tend to cause buildup in the membrane and ultimately increase the necessary operating pressure with time, a cross flow filtration technique will be used instead^[13]. To model this process, empirical relations based on Geankoplis et al.'s *Transport Processes and Separation Process Principles* and Richard W. Baker's *Membrane Technology and Applications* were used in a series of calculations to ultimately determine various necessary parameters, such as inlet flow rate of air and required membrane area for separation. Assuming that the inlet stream is a gaseous binary mixture and given the permeance and selectivity of a chosen membrane material, the composition of the permeate stream can be found using the following equation

$$y_{i,p} = \frac{\phi}{2} \left[y_{i,f} + \frac{1}{\phi} + \frac{1}{\alpha - 1} - \sqrt{\left(y_{i,f} + \frac{1}{\phi} + \frac{1}{\alpha - 1} \right)^2 - \frac{4\alpha y_{i,f}}{\phi(\alpha - 1)}} \right] \quad (1)$$

Where $\phi = P_f / P_p$ is the pressure ratio between the feed and the permeate, $y_{i,f}$ is the molar composition of species i in the feed, and α is the selectivity of the membrane. Using a desired flow rate and purity of desired product in the retentate, a mass balance on each species can be used to determine the flow rate of all three streams, represented via systems of equations

$$\begin{aligned} n_f &= n_p + n_r \\ y_{i,f}n_f &= y_{i,p}n_p + y_{i,r}n_r \\ y_{j,f}n_f &= y_{j,p}n_p + y_{j,r}n_r \end{aligned} \quad (2)$$

where n_p and $y_{i,p}$ denote the total permeate molar flow rate and molar composition of i in the permeate, and the nomenclature is consistent between the all three streams and two species. Along with the mass balance, the molar flux of the permeate stream is needed in order to find the total membrane area required for the desired separation. Assuming that permeation is driven by pressure difference, the permeate flux of species i can be determined using the following expression

$$j_{i,p} = Pe_i (P_{i,f} - P_{i,p}) \quad (3)$$

where Pe_i represents the permeance of species i through the membrane. With both the permeate flow rate and flux, the area of the membrane can be determined using the expression

$$A_m = \frac{n_{i,p}}{j_{i,p}} \quad (4)$$

With this required membrane area and required inlet air flow rate, CAPEX and OPEX of the nitrogen membrane module can be estimated. Example calculations with these series of equations can be found in appendix C.

Ru/C Catalysts for Ammonia Reaction: Kinetics and Thermodynamics

The iron-based catalysts used in the traditional Haber-Bosch process are relatively cheap and capable of achieving high overall conversions, however they require temperatures and pressures up to 600°C and 400 bar. These extreme conditions are energy-intensive but necessary for breaking the nitrogen triple-bond and allowing it to dissociatively adsorb to the catalyst, which is the rate limiting step for the reaction^[14]. Using Ru/C catalysts makes this dissociative adsorption of nitrogen much less energy-intensive and is capable of decreasing the reaction's activation energy by half^[2], allowing the temperatures and pressures to be significantly decreased while maintaining similar conversions. Ammonia synthesis using Ru/C catalysts is an active field of research and has generated numerous models for the reaction kinetics.

The kinetics governing ammonia synthesis have been shown to closely follow a modified Temkin model, which captures both the reversibility of the ammonia reaction and catalyst poisoning due to hydrogen strongly adsorbing to its surface^[2]. Proposed by Yoshida et al., the model takes into account the non-ideal behavior of gasses at very high pressures through the gas activity a_i and fugacity coefficient ϕ_i for each species i . The rate of consumption of nitrogen, and thus the rate of formation of ammonia, is given by the expression

$$r_{N_2} = k_f \frac{\left[(a_{N_2})^{0.5} \frac{(a_{H_2})^{0.375}}{(a_{NH_3})^{0.25}} - \frac{1}{K_a} \frac{(a_{NH_3})^{0.75}}{(a_{H_2})^{1.125}} \right]}{1 + K_{H_2} (a_{H_2})^{0.3} + K_{NH_3} (a_{NH_3})^{0.2}} \quad (5)$$

where $a_i = f_i = \phi_i y_i P$, f_i is the fugacity of species i , y_i is the mole fraction of species i , and P is the total pressure. The reaction rate constant k_f and equilibrium constants K_a , K_{H_2} and K_{NH_3} are given by the equations

$$k_f = 9.02 \times 10^8 \exp \left(-\frac{23,000}{R_c T} \right) \quad (6)$$

$$\log_{10} K_a = -2.691122 \log_{10} T - 5.519265 \times 10^{-5} T \quad (7)$$

$$\ln K_{H_2} = -\frac{56.9024}{R} + \frac{37,656}{RT} \quad (8)$$

$$\ln K_{NH_3} = -\frac{34.7272}{R} + \frac{29,228}{RT} \quad (9)$$

where R is the gas constant in J/mol-K and R_c is the gas constant in cal/mol-K. In order to use the modified Temkin model in an Aspen Plus V12 simulation, Tripodi et al. calculated kinetic parameters to match the format of Aspen's Langmuir-Hinshelwood-Hougen-Watson (LHHW) model^[15], listed in tables 1-3 below.

Table 1. Kinetic parameters for the general ammonia reaction using Ru/C catalysts.

Kinetic Constants		Stoichiometry		
E_a (kcal/mol)	k_o (kmol/s kg-cat.)	N ₂	H ₂	NH ₃
23.0	426	-1	-3	2

Table 2. Kinetic parameters for the LHHW driving force expression.

	Forward Term Exponent	Reverse Term Exponent		Term 1	Term 2
N ₂	0.5	0	A	-7.19	-1.876
H ₂	0.375	-1.125	B	0	-4,609
NH ₃	-0.25	0.75	C	0	2.69
			D	0	1.27E-4

Table 3. Kinetic parameters for the LHHW adsorption expression.

Species/ Coefficient	Term 1	Term 2	Term 3
N ₂	0	0	0
H ₂	0	0.3	0
NH ₃	0	0	0.2
A	0	-10.3	-6.48
B	0	4,529	3,523
C	0	0	0
D	0	0	0

Tripodi et al.'s Aspen simulation also utilized a second kinetic model for at least one of their three reactors in a series of tests between different reactor configurations, however the parameters for the second kinetic model were not listed. The configurations for each equipment block, such as reactor sizing and bed void fractions, were also not listed, making recreating their exact simulation difficult. However, using a test case that had catalyst loading specifications, an approximate recreation was made and the stream results were compared. Using the temperatures and flow rates seen in their Aspen flow sheet, our approximate simulation returned values in relatively high agreement with theirs. Stream temperatures were within an 8% difference between our simulations, and mass flow rates within the ammonia synthesis loop were within a 2% difference. The ammonia product and purge streams, however, had the most deviation between the simulations: our ammonia product stream was 63% that of theirs, and our purge stream was over 600% larger. These discrepancies are likely due to the unknown kinetics of their second model, where changing the compositions of the product streams can have a dramatic effect on the amount of ammonia produced. However, when considering these unknown parameters and the high sensitivity of the process to small fluctuations, these discrepancies were found to be within error, and Tripodi et al.'s Ru/C kinetic model was chosen for our simulation.

Achieving high conversions for the ammonia reaction requires balancing its kinetic and thermodynamic limitations. The reaction achieves its highest equilibrium conversion at low temperatures according to Le Chatelier's principle, but the reaction rate is extremely slow; adding heat will cause the reaction rate to increase dramatically, at the cost of decreasing the equilibrium conversion^[16]. As a consequence, the reaction must always be kept at optimal temperatures in order to maximize the reaction rate and equilibrium conversion. Maintaining these temperatures, however, is difficult because the reaction is exothermic, having an enthalpy of formation $\Delta H_{\text{rxn}} = -45.90 \text{ kJ/mol}$ ^[17]. Once the reaction reaches a certain conversion it will generate enough heat to reduce its equilibrium conversion and slow itself down, preventing it from producing any more ammonia until it can be cooled. This effect is illustrated in figure 2 below: if the inlet temperature to the reactor is too high then the decreased equilibrium conversion will produce less ammonia.

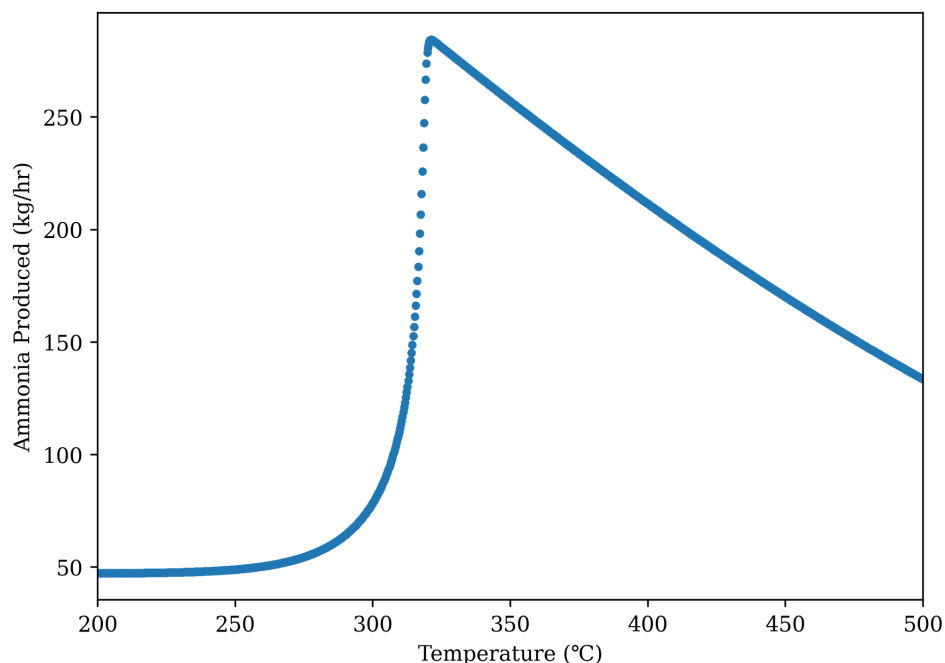


Figure 2. Produced ammonia versus inlet feed temperature for R-101.

This behavior may be observed for two reasons: the high temperatures decreasing the equilibrium conversion of ammonia, and high temperatures promote the desorption of molecules from catalysts^[18]. At the high temperatures within the ammonia synthesis loop, the decreased equilibrium conversion and the increased desorption rate can cause the sharp decline in ammonia production with small changes in inlet temperature.

To accurately model the thermodynamics behind the reaction, the correct property method must be chosen in Aspen. On a molar basis, the system consists mostly of small, nonpolar molecules, lending itself towards the Redlich-Kwong-Soave (RKS) property method; because the process is also operating at high pressures, the Redlich-Kwong-Soave equation of state with the Boston-Mathias function modification (RKS-BM) was the chosen property package for this system^[18]. Other property methods that are valid for this system include Peng-Robinson and Soave-Redlich-Kwong (SRK), as they work well with non-polar or slightly polar systems operating at high temperatures and pressures^[18].

Process Design

Alkaline Electrolyzer

The process currently requires 9,204.3 kg/day of hydrogen gas to be produced. NEL's A3880 electrolyzer produces flow rates of 5,180 kg/day, so two parallel electrolyzers would be needed to meet our required amount of around 10 tons per day^[19]. The parallel A3880 electrolyzers will produce 10,360 kg/day of 99.99% purity hydrogen gas. 1,155.7 kg/day of extra hydrogen gas would be produced which can be sold to cover costs. This is a 17.6 MW electrolyzer with a 25 wt% KOH solution with an assumed conversion efficiency of 90%^[20] to give a mass flow rate of 10,237 kg water/day, or roughly 2,000 gallons per day.

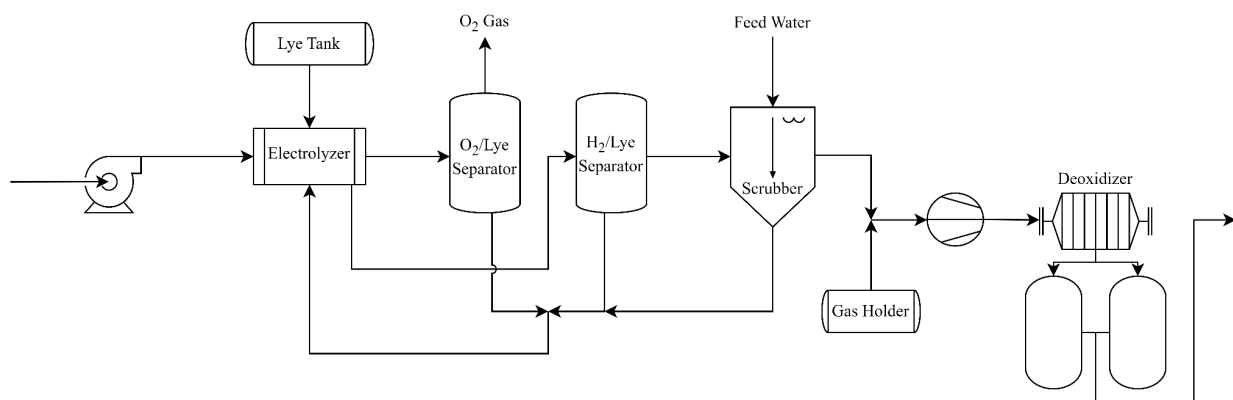


Figure 3. Proposed process flow diagram for electrolysis.

The NEL electrolyzer itself comes with the separators to separate hydrogen, oxygen, and lye. To further purify the stream it is deoxidized in a catalytic reaction. The stream of hydrogen gas is dried in the drying unit below the deoxidizer, which contains a desiccant to absorb water. The scrubber is used to remove any traces of electrolyte from the gas stream, and it is then recycled back into the electrolyzer.

Molecular Membrane Separation Process

The current downstream process for the ammonia production process will require 42.6 metric tons/day of 99.9% purity nitrogen. In order to meet that requirement, our proposed nitrogen production process consists of air that is compressed, chilled, and passed through a single stage membrane, as seen in figure 4.

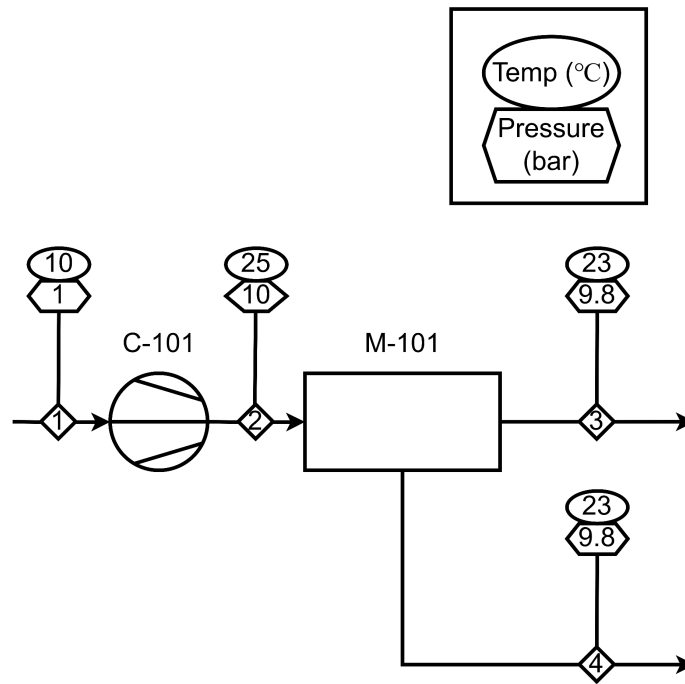


Figure 4. Proposed MMS design for the production of nitrogen.

This design will compress 77.13 metric tons of air per day through C-101 from 1 bar to 10 bar, utilizing a two-stage compressor with intercooling to keep the temperature consistent for the membrane unit. The cooled compressed air stream is then passed through the membrane, separating the nitrogen from oxygen and producing a 99.9% purity nitrogen stream in the retentate (stream 7). According to Bozorg et al., Parker Hannifin's polyphenylene oxide (PPO) membrane module has a permeability of 200 GPU and selectivity of 4.5 at a membrane thickness of 1 μm , thus allowing for optimal separation of nitrogen and oxygen and will be used for M-101^[21]. Once nitrogen passes through the retentate, pressurized vessels will be used to store the nitrogen for usage in the downstream process.

To determine the optimal pressure for this operation, sensitivity analyses were performed on permeate composition and temperature of the outlet stream from C-101, as seen in figure 5.

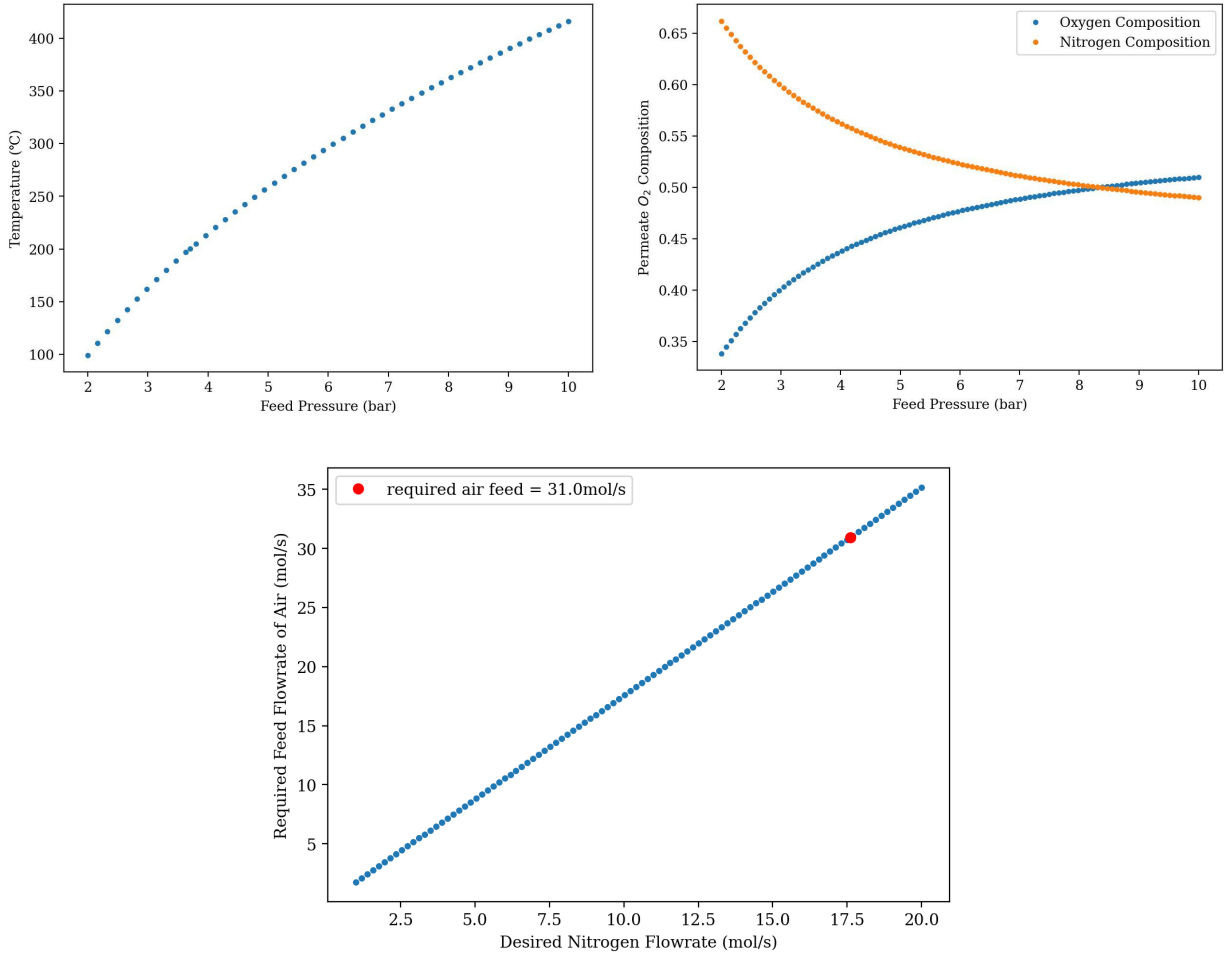


Figure 5. Sensitivity analyses on temperature of C-101 outlet stream with operating pressure (upper left) and permeate oxygen composition (upper right). Both sensitivity analyses were also compared in conjunction with the required air feed flow rate for the required nitrogen flow rate (bottom). Membrane models and sensitivity analyses were created with Python in conjunction with Aspen, as well as equations 1-4. Calculations were made assuming air was ideal at operating conditions and is a mixture of 78% nitrogen and 22% oxygen.

To optimize equipment cost, it was desired to utilize a larger compressor with interstage cooling. It was desired to pressurize air from 1 bar to 10 bar for optimal separation of nitrogen from oxygen as per the membrane module rating, and it was found that this would heat the inlet stream to 416°C assuming air is polytropic, which is much higher than the minimum requirement of 204.0°C for no interstage cooling. Therefore, a multi-stage compressor was used to keep the compressed air stream at a steady 25°C in the membrane. Total required membrane area is 599.6 m², and permeate nitrogen composition was kept at 0.49 to minimize loss of nitrogen to the oxygen waste stream. Although air can be compressed further, the permeate oxygen and nitrogen compositions in figure 5 indicate that the tradeoff would be costly with minimal change in the results, so pressurization was kept at 10 bar. Since the required membrane area is large, the

membrane sheet will be divided into a series of packed membrane tubes, which will then be enclosed in stainless steel 304 for corrosion resistance against oxygen. The membrane module will be constructed similarly to a shell-and-tube heat exchanger, where the permeate will pass through the shell side and the retentate will pass through the tube side. Due to the plateau in oxygen composition of the permeate stream with increasing pressure, as well as the increasing loss of nitrogen retention associated with lower pressures, it was deemed best to pressurize the air stream to 10 bar at the cost of a larger compressor with a smaller total membrane area.

Reactor Sizing Through Sensitivity Analyses

To determine an optimal size for the PBR in the downstream ammonia synthesis loop, sensitivity analyses were performed for the effects of length on the reaction at a pre-specified diameter. As the length of the reactor increases the amount of ammonia produced plateaus due to the decreased equilibrium conversion at higher temperatures, so oversizing the reactor will not produce more ammonia. This effect is illustrated in the sensitivity analysis in figure 7 below.

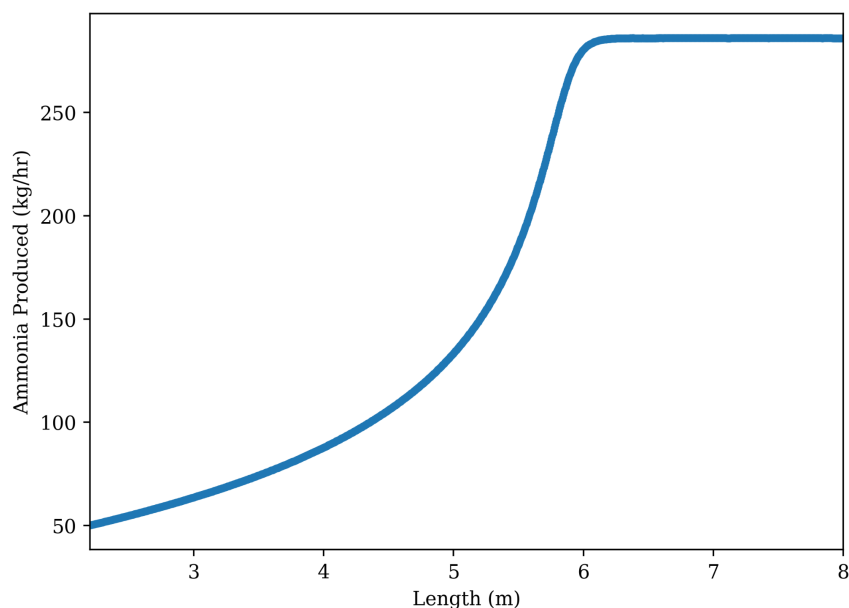


Figure 7. Produced ammonia versus length of R-201. Diameter is 2 meters.

It was found that a diameter larger than 2 meters had a negligible effect on production rates, and anything smaller would cause the length of the reactor to be larger than 10 meters. Though this length of reactor is possible, decreasing it would make transportation and cleaning much easier. A sensitivity analysis for the length of R-201 indicates that having a diameter of 2 meters and a length of 6 meters would be the optimal configuration.

The inlet temperature to the reactor should be high enough to reach the ignition point of the reaction, but should not exceed 400°C to maximize the conversion. According to figure 15 of the appendix, temperatures past ~320°C would cause the conversion to ammonia to decrease significantly. Also, temperatures below ~250°C will exceed the extinction point of the reaction, preventing it from heating itself. This gives an inlet temperature range for R-201 of 310-320°C.

In order to withstand the high reaction temperatures and resist unwanted corrosion or oxidation, the reactors were constructed using stainless steel 304. Hydrogen, at high temperatures and pressures, is capable of diffusing into metals like carbon steel and displacing atoms, forming a porous structure that has a decreased structural integrity^[21] in a process known as high-temperature hydrogen attack. Stainless steel 304, along with other types of stainless steel or alloy steel, are less susceptible to embrittlement because of their high tensile strength, and can thus resist the effects of hydrogen diffusion within the metal lattice^[22].

Flash Separator Sizing Through Sensitivity Analyses

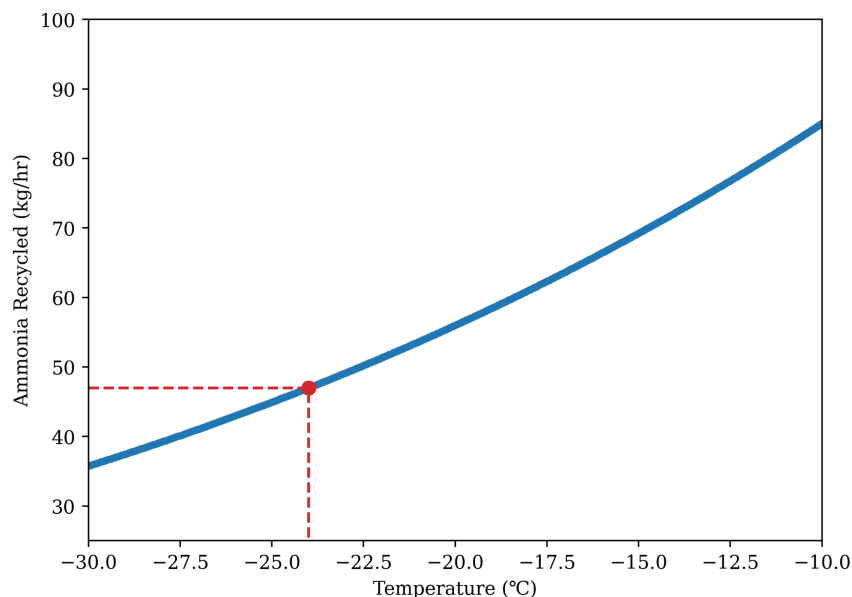


Figure 8. Recycled ammonia versus flash temperature in V-201. Pressure is 98.7 bar.

A flash drum after the second reactor will be used to separate ammonia from unreacted hydrogen and nitrogen. Ammonia has a higher flash point than hydrogen and nitrogen at 98.7 bar, allowing it to be separated in a liquid stream at 99.8 wt% and -24°C. Furthermore, limiting the amount of ammonia in the recycle stream was one of the constraints of this process because having too much ammonia in recycle will lower how optimal the production of ammonia is because it competes for active sites on the catalyst with nitrogen and hydrogen. The process recycles approximately 47.2 kg/hr per process of ammonia which is 10.9% of the produced amount from the reactor. The process creates 2,155.7 kg/hr of ammonia, which slightly exceeds the 50 metric ton/day constraint. The flash separator was sized based on heuristics and also made of stainless

steel 304 to mitigate hydrogen embrittlement. The flash separator should have a 2-foot diameter and be 10 feet tall, with a 2-inch thick shell and 3.33-inch thick elliptical heads.

Accounting for Pressure Drop

The pressure drop across each reactor was estimated after they had been sized using a combination of the Ergun pressure drop equation and a kinetic energy balance for reactive systems. The Ergun equation in differential form is given by

$$\frac{dP}{dz} = \frac{(\phi - 1)Q}{D_p A_c \phi^3} \left[\frac{150\mu(1 - \phi)}{D_p} + \frac{1.75\rho Q}{A_c} \right] \left[\frac{P_o T(1 - \varepsilon X)}{P T_o} \right] \quad (10)$$

where P is the pressure along the length of the reactor z , ϕ is the void fraction, Q is the volumetric flow rate of reactant, D_p is the catalyst diameter, ρ is the density of the reactants, A_c is the cross-sectional area of the reactor, μ is the viscosity of the vapor, P_o is the inlet pressure, ε is the relative change in moles, X is the conversion, T_o is the inlet temperature and T is the outlet temperature. The outlet temperature was calculated using the chemical kinetics energy balance given by

$$T = \frac{-X\Delta H_{rxn}^o + \sum C_{P,i}T_o\theta_i + X\Delta C_P T_R}{\sum C_{P,i}\theta_i + X\Delta C_P} \quad (11)$$

where ΔH_{rxn}^o is the enthalpy of formation of ammonia, $C_{P,i}$ is the heat capacity of species i , θ_i is the stoichiometric coefficient of species i , ΔC_P is the change in heat capacity between reactants and products and T_R is the temperature of the reactor.

When the Ergun and energy balance equations are used in tandem, they provide an estimate for the pressure drop in systems where the packed bed decreases pressure but the exothermic reaction expands the gas. For this calculation we chose $\phi = 0.5^{[23]}$, $D_p = 5 \text{ mm}^{[24]}$, and $\mu = 0.0183 \text{ cP}^{[25]}$ (approximated as the viscosity of hydrogen gas). This estimates the pressure drop across R-201 to be 0.961 bar, and a sensitivity analysis for this is visualized in figure 9. These values were specified in Aspen to more accurately model the reactor.



The diagram illustrates a chemical process flow involving nitrogen (N₂) and hydrogen (H₂) feed streams. The process includes two compressors (C-201, C-202), three heat exchangers (E-201, E-202, E-203), a reactor (R-201), and a separator (V-201). The flow is characterized by 14 numbered nodes and 14 labeled streams, each with associated temperature and pressure data.

Legend:

- Temp (°C): Oval symbol
- Pressure (bar): Hexagon symbol

Process Flow Details:

- Feed Streams:** N₂ and H₂ feed into Node 1 (Temp: 25°C, Pressure: 1 bar).
- Compression:** The feed is compressed by C-201 to Node 2 (Temp: 13°C, Pressure: 100 bar).
- Heat Recovery:** The compressed feed is preheated in E-201 by a stream from Node 3 (Temp: 319°C, Pressure: 99 bar) to Node 5 (Temp: 149°C, Pressure: 98 bar).
- Reaction:** The preheated feed enters the reactor R-201 at Node 4 (Temp: 466°C, Pressure: 98 bar).
- Separation:** The reactor effluent is separated in V-201. The bottom product (Node 8, Temp: -24°C, Pressure: 99 bar) is recycled back to Node 1. The top product (Node 9, Temp: -24°C, Pressure: 99 bar) is recycled back to Node 2.
- Heat Recovery (Continued):** The reactor effluent is cooled in E-202 by a stream from Node 6 (Temp: 107°C, Pressure: 1 bar) to Node 11 (Temp: 7°C, Pressure: 1 bar). The cooled stream then enters E-203, which is cooled by a stream from Node 13 (Temp: -45°C, Pressure: 1 bar) to Node 14 (Temp: 6°C, Pressure: 1 bar).

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Our proposed process is a modified Haber-Bosch process that uses Ru/C catalysts which are capable of decreasing the temperature and pressure requirements significantly. The process uses an adiabatic packed bed reactor made of stainless steel 304 with a series of heat exchangers that use the least amount of utilities for optimal cooling. The process begins with a centrifugal compressor (C-201) from Atlas Copco^[26] with an inlet feed of 3:1 hydrogen-nitrogen molar ratio that compresses the stream to 100 bar and a volumetric flow rate of 103.5 m³/hr. Interstage cooling is required to prevent damage to the compressor from the high temperatures generated through polytropic compression. The compressed stream mixes with a recycle stream and flows into a shell and tube heat exchanger (E-201) on the shell side and brings it to 319°C. The heated stream enters a 6-meter long and 2-meter diameter PBR (R-201), through which there is a 0.961 bar pressure drop. The stream gets heated to 466°C from the exothermic reaction within R-201, and is immediately cooled to 149°C after passing through the tube side of E-201 to heat up the inlet stream. The stream then passes through two heat exchangers: the first one (E-202) is driven by cooling water at 7°C that cools the stream to 17°C, and the second (E-203) is driven by liquid ammonia at -45°C that cools the stream to -24°C. The liquid ammonia gets recycled back to an LN-60W chiller unit^[27] to be cooled back to -45°C, and the cooled product stream enters a flash drum to separate the liquid ammonia from unreacted gaseous hydrogen and nitrogen. The 99.8 wt% liquid ammonia product is sent to a storage tank and the unreacted hydrogen and nitrogen are recycled with the process inlet stream.

Process Economic Analysis

A key consideration for the viability of our zero emission ammonia plant was economic viability. As a result, an economic forecast based on a twenty-year plant life span was performed based on preliminary manufacturing and capital costs. A cash flow diagram has been created to analyze different profitability models of the plants net present value (NPV), discounted cash flow rate of return (DCFRROR), modified internal rate of return (MIRR) , and before tax return on investment (BTROI). The Minnesota corporate tax rate was found to be 9.8%, the reinvestment rate to be 10%, and an inflation rate of 3% was assumed for the purpose of discounted cash flow calculations.

Several calculation assumptions were implemented to perform our economic analysis. A conservative 5% production down time was assumed due to maintenance, replenishment of the catalyst beds etc. Salvage costs of all equipment were assumed to be zero. A capital depreciation schedule of 5, 7 and 10 year MACRS were compared, beginning at the end of a 3 year installation period. The plant has an estimated on-stream factor of 95%, corresponding to 347 days of operation annually. The sales price of ammonia was based on an average \$1100 per metric ton. Similarly, calculations used the ruthenium catalyst cost of \$500 per kilogram. Lastly, since an area clientele consists solely of farmers, a raw water treatment plant is assumed to be already installed within serviceable range of the plant. Lastly, because the process produces green hydrogen, the Inflation Reduction Act^[28] allows for up to \$3 of tax credit per kilogram of green hydrogen produced for up to ten years, providing \$10,950,000 of tax credit annually which is based on a hydrogen production rate of 10 metric tons per a day. As a result, for the first ten years of operation the process is essentially tax free.

Total Capital Investment:

Based on equipment specifications determined previously, the equipment was priced based on cost correlation charts and bare modulus methods with a CEPCI, correlating to April of 2023, of 800.6^[29]. Due to its corrosive resistance to hydrogen, stainless steel was used for the material of construction of the ammonia synthesis process as well as the hydrogen production process. Carbon steel was used for the remaining equipment due the affordability and reliance under standard operating conditions. The capital investment of the entire plant was estimated using the methodology described in Turton's *Analysis, synthesis and design of Chemical Processes*^[30]. Similarly, the equipment costs were estimated using parameter cost correlation data and bare module cost methodology^[30]. Equipment costs are shown in Appendix B, Table 14.

The fixed capital investment (FCI), or grass roots cost, was found to be \$38,725,172 based on the 18% increase of the summation of the bare module costs of the ammonia synthesis loop, the hydrogen synthesis, and the nitrogen synthesis plus half of the base bare module costs as an

estimation of the outside battery limit (OSBL) costs. The ISBL, which accounts for the total bare module costs, was found to be \$25.49 million. Table 4 below details the equipment bare module cost breakdown. Respective process equipment bare module costs are shown in appendix B, table 14.

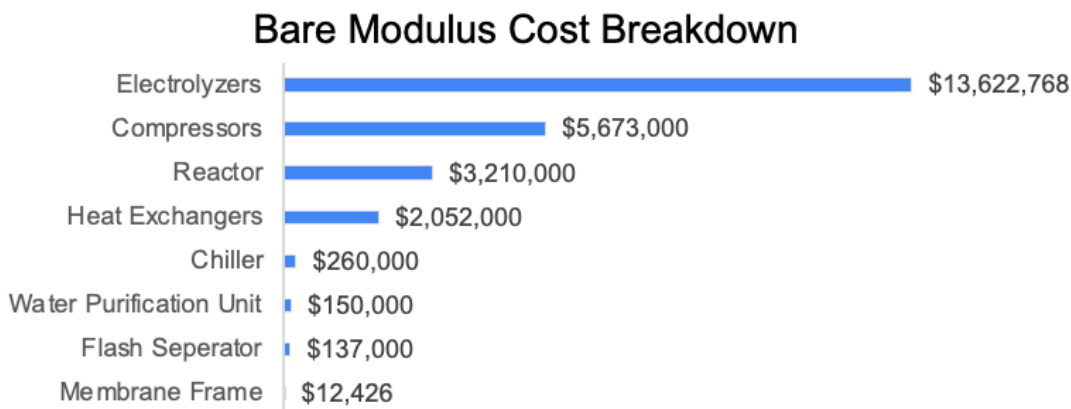


Figure 11. Process Equipment Cost Distribution

To calculate the working capital, the sum of the costs of chemical reagents, operating labor, storage infrastructure for products and reactants, and necessary utilities all need to be taken into account. The labor required was determined based on equation 43 in the appendix. The process required no solid particulate handling steps and 21 processing steps are required for the entire ammonia chemical process. An additional operator for the nitrogen synthesis and hydrogen synthesis process increases the total number of operators to 3. For an annual operating salary of \$70,000, the cost of operating labor was estimated to be \$950,000. The working capital was calculated to be \$ 2,861,958, and was derived from the sum of the costs of chemical reagents, ruthenium catalyst costs, membrane replacement costs, operating labor, and wind farm utility costs. The water requirement of the process is derived entirely from groundwater and therefore not included in the utility costs. As a result, the total capital investment (TCI), which is the sum of the working capital and the FCI, was estimated at \$38,725,172.

The cost of manufacturing (COM) is a summation of the fixed, the direct, and general manufacturing costs. To determine the direct manufacturing costs, the costs of raw materials and utilities need to be determined. Leasing wind farm electrical utilities for \$700 per kilowatt, the estimated cost of operation was determined to be a minimum of \$18,000,000 over the course of 20 years, averaging to \$1,058,823 annually. The water required in the entire process was estimated to be 40 million gallons annually, which corresponds to a \$140 groundwater drawing permit^[31] since the water groundwater draw rate falls below the 50 million gallon annual bracket. Furthermore, the Ruthenium catalyst replacement costs were estimated to be \$500 per a kilogram with an average poisoning rate of 0.1 kilograms per a metric ton of ammonia produced, resulting in an annual cost of \$821,250. In comparison, the nitrogen synthesis PPO membrane had an

estimated replacement schedule of 6-10 years, rounding to a total of 3 replacements over 20 years, equalling \$4,235 annually. As stated previously, the estimated operating labor cost for 3 shifts and a salary of \$70,000 is \$945,000.

The direct supervisory and clerical labor was estimated to be 18% of the operating costs and the laboratory costs were estimated to be 15% of the operating costs. The cost of maintenance and repairs was estimated to be 6% of the FCI, costing \$2,323,510. The patents and royalties were equivalent to 3% of the COM, costing \$429,639. With these results, the COM was determined to be \$14,321,318.

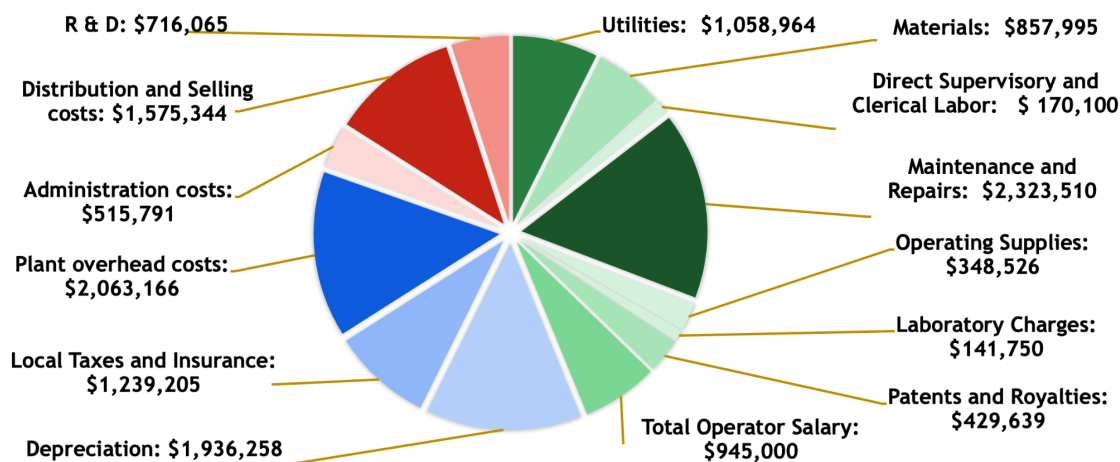


Figure 10: Cost of Manufacturing breakdown

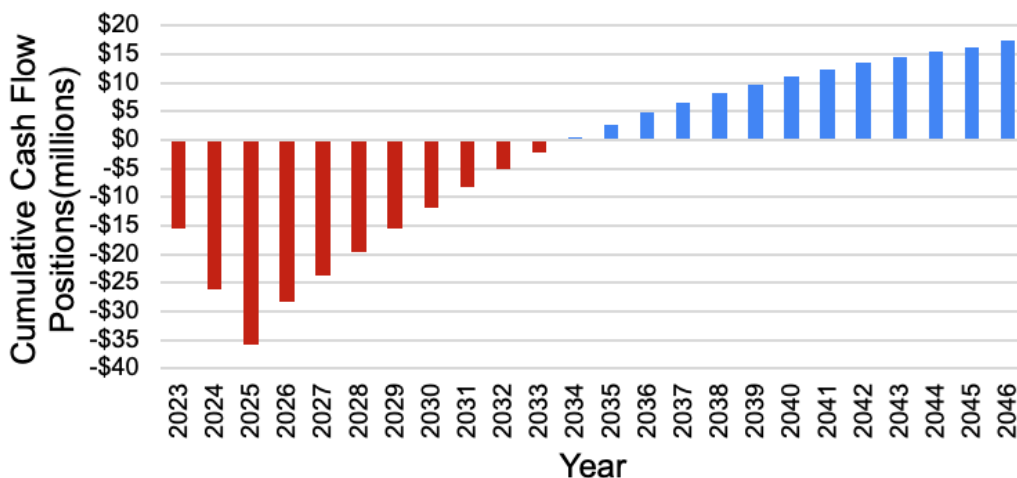


Figure 12. Cumulative Cash Flow Position over a 20 year plant lifespan and a 10-year MACRS depreciation schedule.

The working capital was invested in the third year and 40% fixed capital investment was invested in year one, and 30% invested in the second and third year.

Profitability Measures

To determine the economic viability of the plant, several economic considerations were analyzed. One method was to determine the most favorable depreciation schedule for our equipment. Since the lifespan of our equipment, with sufficient maintenance, can last longer than the intended 20-year lifespan of our plant, a longer depreciation schedule was expected to be more beneficial. Shown below is a comparison table of the different MACRS depreciation schedules.

Table 5. Depreciation Schedules

MACRS Schedule	BTROI %	DCFROR %	MIRR	NPV (\$ in millions)
5 year	24.9	14.78	14.80	16.07
7 year	24.9	14.89	14.88	16.36
10 year	24.9	15.60	15.00	17.39

The BTROI is a measure of the return investors can expect over the lifespan of the plant and is defined as the difference between the total sales and the operating costs divided by the total capital investment. Similarly, the net positive value (NPV) represents the expected profit over the entire duration of the plant's life span. As a result, the most economical MACRS schedule is the 10-year schedule as it saves approximately \$1 million in capital. With this schedule, the NPV was found to be \$17.39 million and the MIRR, which assumes the positive cash flows are reinvested in the project's capital costs, has a value of 15.00%, which signifies a market competitive, profitable venture. Detailed economic parameters are listed in table 6 below.

Table 6. Capital Expenditures

Expenditure	Cost (\$ in millions)
Fixed Capital Investment	38,725,172
Working Capital	2,861,958
Total Capital Investment	41,587,131
Cost Of Manufacturing	14,321,318
BTROI %	24.9

Expenditure	Cost (\$ in millions)
Fixed Capital Investment	38,725,172
DCFRROR%	15.60
MIRR%	15.00
NPV (\$ in millions)	17.39

Product Price and Capital Investment Sensitivity

Since the operational utilities are self-sufficient due to feed streams being derived from on site natural resources, plant economic variation was found to be subject primarily to the sales price of ammonia, the ruthenium catalyst cost, the cost of the electrolyzers, and the Minnesota corporate tax rate. The breakeven values for these metrics and their corresponding variation percent is listed below.

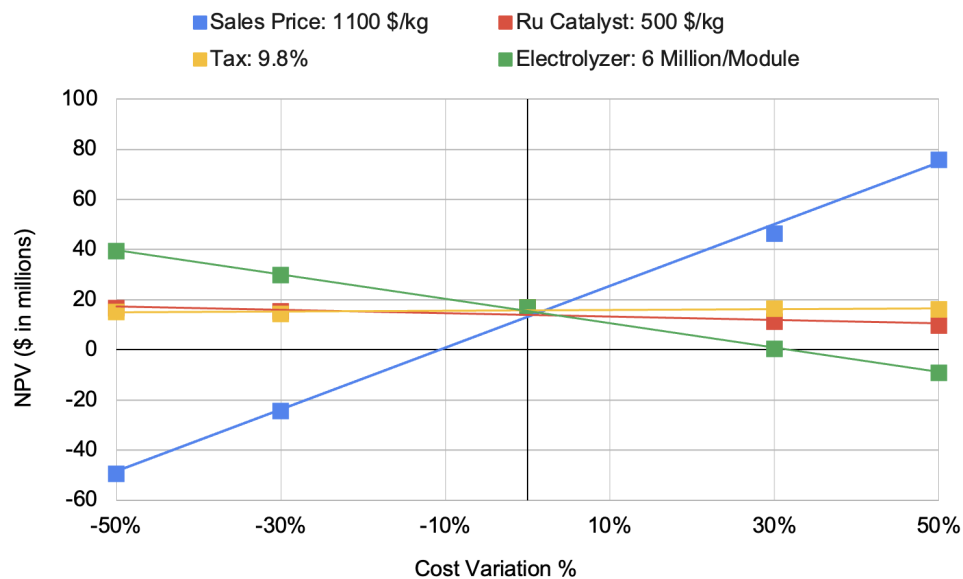


Figure 13. Cost variation of 50% to analyze NPV of Ammonia production system.

Table 7: Sensitivity and Economic Metrics

Parameter	Breakeven (%)	Breakeven Value	Current Value
Sales Price	-12.1	\$966	\$1100
Ru Catalyst	+318	\$1590	\$500

Tax	+1200	117 %	9.8 %
Electrolyzers	+33.3	\$16.5M	\$12.0M

As shown in Figure 13, the ammonia break even value of 966 \$/kg requires a variation of -12.1% in the 1100 \$/kg price, indicating the reliance of the NPV, and thus the economic viability on the ammonia sales price. Furthermore, a DCFROR does not become equivalent to 15% until a -3% decrease in ammonia sales price, equivalent to 1067 \$/kg. Recently, ammonia sales prices have increased drastically due to a shortage of supply chains, resulting in a higher current sales prices. However, as supply chains reopen, a more accurate ammonia sales price assessment would be of the original sales price accounting for inflation, which rests at roughly 1100 \$/kg^[32]. Since the operation of the plant is over a long duration, the highsmall variance fluctuations in sales make a significant impact on the viability of the plant. As shown above, the high variation percent in the catalyst cost and corporate tax rate, 318% and 1200% respectively, prove the process NPV be fairly robust, such that even if the tax rate increases significantly or the ruthenium catalyst becomes scarce, the NPV will not be affected significantly.

Overall, the process economics project a profitable investment, however the economic prediction methods are -20% to +30%. As a result, the TSC recommends more rigorous estimates from contractors or financial specialists to more accurately forecast the process's profitability.

Environmental, Health, and Safety Considerations

Environmental Impacts

In our modular ammonia production process design, many of the decisions were based on ultimate the goal of carbon neutrality. Starting with the upstream process, nitrogen and hydrogen production both employ methods that require no burning of fossil fuels. Stepping away from the traditional SMR and WGS reactions, our NEL electrolysis unit for hydrogen production requires no fossil fuels. Although energy duties for the electrolysis process are high, it can be powered from sustainable resources, such as solar or wind power. Nitrogen, moreover, utilizes MMS as its primary process for nitrogen production. When compared to traditional PSA and CD systems, it was found that MMS was the least energy intensive process while maintaining nitrogen production quality due to the differences in the required operating pressures. Additionally, due to the lightweight nature of MMS equipment versus PSA and CD equipment, transportation duties and associated emissions will also be reduced when shipping to point-of-use locations. Ease of transportation for equipment coupled with zero emissions of carbon dioxide make both of these processes viable for the production of hydrogen and nitrogen.

Not only was the upstream process designed for sustainability, but numerous changes and improvements have also been made to our downstream ammonia production process to promote safety and sustainability. With the usage of an Ru/C catalyst, operating temperatures and pressures have been lowered in comparison to the iron-based catalyst for the traditional Haber-Bosch process. As previously mentioned, traditional Haber-Bosch processes typically operate at pressures of 200-400 bar and temperatures of 400-600°C, with the overall process contributing to approximately 2% of global fossil fuel consumption annually^[1]. Preliminary results when utilizing the Ru/C based catalyst, however, suggested operating pressures and temperatures would decrease by about 50-200 bar and 50-100°C, respectively. The utilization of an Ru/C catalyst will not only significantly decrease capital and operating costs for the production of ammonia, but it will lessen the energy requirements for the process overall.

Health Impacts

Throughout the ammonia synthesis process, various health risks were identified in both upstream and downstream processes, and mitigation steps were taken to protect the health and safety of the operators. A list of health risks and corresponding mitigation steps can be found in the table below.

Table 7. Various health risks and mitigation steps associated with our ammonia production process.

Associated Processes	Health Risks	Mitigation Steps
Hydrogen Synthesis	Electrolysis cells can be an electrical hazard for operators if wires are exposed.	Proper PPE will be worn when handling electrolysis cells (i.e., wearing electrically insulated rubber gloves, etc.).
	Hydrogen gas intake can irritate lungs and potentially displace air in a room, causing operators to have shortness of breath and dizziness ^[33] .	Place various pressure gauges on hydrogen storage tanks and gas detectors on the NEL electrolyzer unit to detect potential hydrogen leakage ^[33] .
	Potassium hydroxide, the electrolyte in the NEL electrolyzer unit, can cause chemical burns if it comes into contact with the skin or eyes. Breathing potassium hydroxide vapors can irritate lungs ^[34] .	Proper PPE will be worn when handling the concentrated potassium hydroxide. The NEL electrolyzer unit will be checked monthly for spills and leakage.
Nitrogen Synthesis	Nitrogen can displace the air in a room and cause operators to have shortness of breath and dizziness. Rapid expansion of compressed nitrogen can also cause burns and frostbite ^[35] .	Gas detectors and pressure gauges will be implemented throughout the process to monitor the nitrogen pressure and allow for operators to respond accordingly if a leak were to occur. Gaskets will be present throughout piping to prevent leakage of nitrogen gas.
Ammonia Synthesis	Gaseous ammonia is toxic with an LC50 inhalation of 4.93 mg/L. It is also highly reactive with water and can cause chemical burns, especially if it comes into contact with the skin or eyes ^[36] .	Proper PPE will be worn by operators when handling ammonia. Gaskets will be implemented throughout reactor modules and piping to prevent exposure. Gas detectors and pressure gauges will be implemented throughout the process to ensure proper awareness of ammonia gas leakage and allow for adequate time to respond. 99.9% purity nitrogen and hydrogen will be fed through the process to

decrease potential water vapor that could mix with ammonia. Monthly health screenings will be implemented to look for signs of ammonia-related health issues, such as newly developed ammonia-induced alveolar edema^[36].

Ru/C catalyst can decompose into ruthenium oxide, a known eye and skin irritant. Moreover, it is a known carcinogen and can be toxic to aquatic life^[37].

Proper PPE will be worn by operators when handling Ru/C catalysts. Spent Ru/C catalyst will be contained in labeled steel drums and removed from the site once filled, preventing any further exposure from the operators. Containers of spent catalyst will be kept away from bodies of water with aquatic wildlife^[38].

Chemical Compatibility

The safety of a chemical plant heavily relies on the reactivity of all species involved. Regardless of whether the species are expected to come into contact with each other or not, it is important to understand the outcome should they come into contact. Determining possible reaction outcomes can be done using chemical compatibility tables, which lists each species' hazards (health, flammability, instability and special properties) and any reactivity with other species. The chemical compatibility table for the modular ammonia plant was made using the AIChE Chemical Reactivity Worksheet (CRW)^[39] and is presented in figure 14 below.

Y

N

C

SR

: Compatible

: Incompatible

: Caution

: Self-Reactive

*

: Changed by user

NFPA				Modular Ammonia Plant Compatibility Chart	AMMONIA, ANHYDROUS	CARBON DIOXIDE	NITROGEN	OXYGEN	POTASSIUM HYDROXIDE, SOLUTION	WATER
Health	Flammability	Instability	Special							
3	1	0		AMMONIA, ANHYDROUS						
				CARBON DIOXIDE	Y					
				NITROGEN	Y	Y				
3	0	0	Oxi	OXYGEN	N	Y	Y			
3	0	1		POTASSIUM HYDROXIDE, SOLUTION	C	Y	Y	N		
				WATER	C	Y	Y	N	C	

Figure 14. Chemical compatibility table for all species involved in the plant.

From the table, most of the species involved in the process are compatible with each other and do not pose an immediate hazard when in contact. Some chemical pairs, such as oxygen-ammonia and potassium hydroxide-oxygen, react to produce a corrosive compound or take part in potentially unwanted exothermic reactions, respectively. Several processes were designed with chemical compatibility in mind to address these possible hazards. The electrolyzer and MMS processes are able to achieve very high purities (>99.9%) of hydrogen and nitrogen respectively, reducing the chance that oxygen or other impurities can enter the ammonia process and potentially cause an explosion or corrode the equipment. For most of the plant's operation, the heat exchangers are driven by the exothermic reactions in the reactors, nearly entirely removing the need to introduce steam into the system that can seep through gaskets and enter the system.

Inherently Safer Design

Chemical plants utilize several compounds and equipment that, when not handled properly, can introduce hazards and cause possibly fatal injuries or cost millions of dollars in repairs. To avoid this, the plant must be constructed with inherently safer design in mind. There are four categories in which a plant or process can be evaluated based on inherently safer design: (1) minimize or intensify the use of hazardous compounds or operate at less extreme conditions, (2) substitute hazardous chemicals or unit operations with less hazardous ones, (3) moderate the use of hazardous chemicals or equipment, and (4) simplify the process by eliminating unnecessary complexity.

Our proposed design, being several times smaller than stick-built ammonia plants, is already inherently safer as it contains less of the potentially hazardous materials and in a tightly contained system. To make the process even more safe, however, the interchangeability of modules can foster the use of smaller reactors, heat exchangers, and flash drums for farms that require less than 50 tons of ammonia per day. The smaller equipment will pose less of a hazard by physically containing less material, and the farm can use less electrical energy, cooling water, and liquid ammonia.

The use of Ru/C catalysts requires temperatures roughly 100°C cooler and pressures 100 bar less than the traditional Haber-Bosch process. The lower temperatures and pressures reduce the likelihood that a reactor, flash drum, or pipes and fittings rupture, leak, or otherwise fail. The modular design of the process also aids in reducing hazards: should a piece of equipment rupture or leak, it would likely occur in only one of the five separate ammonia synthesis loops, causing the hazard to be a fraction of what it would be if it were all one process. Upstream of the ammonia synthesis loop, MMS is capable of producing nitrogen at 4 bar and 200°C – compared to other common sources of nitrogen such as PSA, which operates at 10-40 bar, MMS has a lower risk of rupturing a vessel and releasing potentially explosive oxygen into the surroundings.

Being small-scale, our proposed design is capable of utilizing electrolyzers instead of the common large-scale approach to sourcing hydrogen, such as SMR. SMR operates at conditions up to 25 bar and 1,000°C^[3], posing a serious risk for burns to operators and wildlife. SMR also requires burning fossil fuels because of the high duties for those operating conditions to be reached. Electrolysis, on the other hand, can operate at atmospheric temperatures and pressures, negating the risk for burns or possible vessel rupture. Utilizing electrolysis substitutes the fossil fuel requirement with electricity, which can be sourced from wind or hydroelectric power.

The lower temperature and pressure requirement for using Ru/C catalysts allows our proposed process to simplify the Haber-Bosch process. Usually requiring three reactors^[40], our process can achieve similar conversions using two reactors; if reactor cooling is implemented, it may be possible to reduce it to one reactor. This simplification reduces the number of pipes, fittings, and other peripheral equipment that may fail and cause a rupture or leak. Similarly, the MMS process upstream replaces PSA, which utilizes multiple columns and periodic pressure changes, with a single multi-stage compressor and membrane separator unit. Reducing the number of moving parts and operating condition changes can reduce the likelihood that one part of the system can fail.

HAZOP Study

Understanding the high level hazards of the entire process can aid in making safety protocols and informing us on where additional safeguards need to be put in place. To do this, a hazard and operability (HAZOP) study was performed around the reactor R-201, the piece of equipment that was believed to have the most extreme consequences if something were to go wrong, including rupture and explosion. The study focused on deviations in the inlet flow rate, temperature, and pressure and their consequences, and is listed in table 8 below.

Table 8. HAZOP analysis for reactor R-201.

Deviation	Guide Word	Cause	Consequence	Action
Inlet Flow	No	Heat exchanger H-201 is clogged	Heat exchanger is overpressurized, greater chance of explosion	Implement a pressure relief device
			Compressed H ₂ and N ₂ in stream 1 will travel down the RECYCLE2 stream	Check valve on the RECYCLE2 stream
	Less of	Malfunction of upstream nitrogen or hydrogen process	Decreased inlet pressure with possibility of back flow of ammonia	Implement controls to equalize pressure by sending vapor to a storage tank to avoid backflow
	More of	Downstream cooling heat exchangers malfunction, sending more vapor through recycle stream	Buildup of pressure and vapor in system, greater chance of explosion	Implement a pressure relief device
Temperature	Less of	Heat exchanger H-201 is too cold	Ignition temperature may not be reached and reaction will not start	Check temperature, heat inlet with steam
	More of	Downstream cooling heat exchangers malfunction, sending hotter vapor through recycle stream	Reaction conversion will decrease with excessive heat	Check temperature, increase coolant flow rate Include bypass streams to redirect high-temp vapor

Pressure	Less of	Leakage of reactor components	Flammable hydrogen and toxic ammonia gas will be released	Ventilate and/or evacuate area; require PPE in plant vicinity
	More of	Downstream of the reactor becomes clogged or broken	Reaction conversion increases, greater chance of explosion	Implement a pressure relief device to send vapor to a storage tank, shut off the upstream processes

The main consequences for the process were either rupture/explosion of R-201, or backflow through the recycle stream that can damage C-202. Implementing pressure relief devices (PRD's), pressure controllers that can send vapor to a storage tank, and temperature controllers to increase coolant flow rate were the safeguards that were most applicable to a variety of situations. We recommend implementing PRD's and pressure and temperature controllers to mitigate any possibility that R-201 will rupture/explode, regardless of their probability. Performing a more intensive and quantitative safety analysis, such as a fault tree or event tree analysis, can provide deeper insight on the probability that a rupture/explosion will occur and how additional safeguards can decrease the probability further.

In the case that R-201 does rupture/explode we recommend fitting the entire plant with a sprinkler system if it is placed within a building, or a deluge system if it is outdoors to put out any fires that may have started. Because the high pressures within the system can cause a more dangerous explosion compared to lower pressures, we recommend that the equipment also be designed to be explosion-proof. The CDC recommends encasing vulnerable or at-risk equipment with an explosion proof box that is certified by the National Institute for Occupational Safety and Health (NIOSH) and International Electrotechnical Commission (IEC)^[41]. In accordance with inherently safer design, the plant should also be placed far away from any residence or office building, as it is common for explosion debris to travel miles from the blast^[42].

Conclusions and Recommendations

In conclusion, the modular ammonia synthesis plant consisted of an upstream process consisting of water electrolysis for hydrogen gas, and a membrane separation for nitrogen and a downstream process of a modified Haber-Bosch process with a Ru/C catalyst to achieve lower pressures and temperatures. The process utilizes groundwater sources in Minnesota for cooling, and the electrolyzer, and a wind farm to power the process electrically. The design achieves our goal of practically entirely green operation while producing 51 tons of 99.8 wt% ammonia per day. Overall, despite the high capital investment, the process economics projects a profitable venture with a competitive return on investment, allowing for the economic viability of the plant over a 20 year lifespan. Further research needs to be done to produce hydrogen gas electrically more efficiently with less energy requirements. Furthermore, more research needs to be done into separating ammonia from nitrogen and hydrogen gas at lower pressures more efficiently to decrease the costs of the process further. Reducing the amount of energy usage would inadvertently reduce the cost of the wind farm. The process was found to be much more environmentally conscious compared to large-scale Haber-Bosch by using renewable energy, and is inherently safer due to the less extreme operating conditions. The plant still operates at high temperatures and pressures, so additional preventative safeguards such as pressure relief devices, pressure controllers, and temperature controllers are recommended to be implemented. Mitigative safeguards such as sprinkler/deluge systems and explosion proof boxes are also recommended to reduce the damage caused by fires and explosion debris.

Acknowledgements

We would like to acknowledge and thank Professor Matthew Ellis for assisting us in the production and approach of this grand undertaking. This project would not have been possible without his guidance and teaching.

We would also like to thank all of the professors and staff at the Chemical Engineering department of UC Davis for teaching us all the concepts necessary to this project, as well as providing the Aspen Plus V12 software for us to model the process design.

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Appendix

Appendix A - Additional Figures

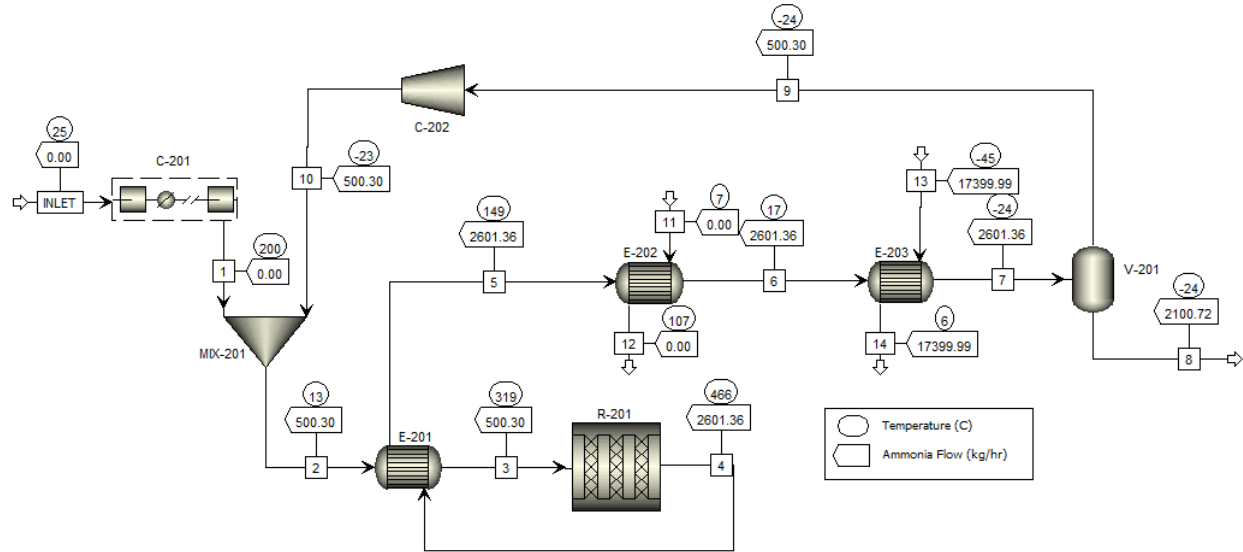


Figure 17. Aspen flowsheet of the ammonia synthesis loop.

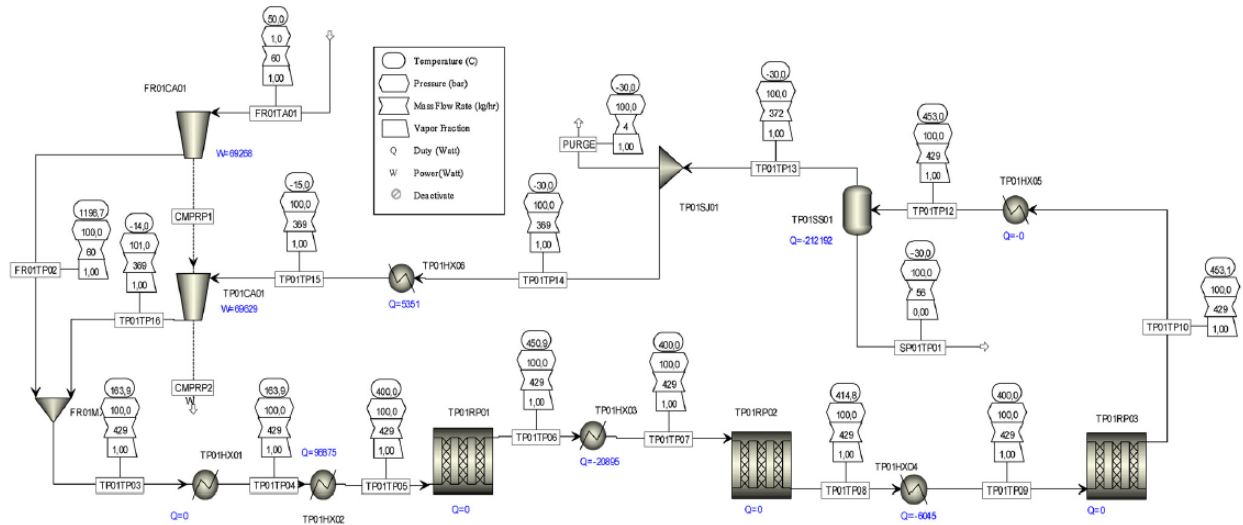


Figure 18. Aspen flowsheet from the paper by Tripodi et al.

Appendix B - Additional Tables

Table 8. Material Balance for M-101

Stream	n (mol/s)	n_{N_2} (mol/s)	n_{O_2} (mol/s)	y_{N_2} (mol/mol)	y_{O_2} (mol/mol)
Feed, f	30.94	28.20	7.95	0.780	0.220
Permeate, p	13.31	6.52	6.79	0.490	0.510
Retentate, r	17.63	17.61	0.02	0.999	0.001

Table 9. Reactor configurations and catalyst properties.

Parameter	R-201
Reactor Type	Adiabatic PBR
Length (m)	6
Diameter (m)	2
Particle Density (kg/m ³)	590
Bed Voidage	0.5

Table 10. Heat exchanger configurations.

Parameter	H-201	H-202	H-203
Exchanger Area (m ²)	26.13	522.3	195.3
Tubes	93	1,125	277
Tube Passes	1	1	1
Tube Length (m)	4.8	4.05	6
Shell ID / OD (m)	0.3 / 0.344	0.875 / 0.969	0.450 / 0.496
Material	SS-304	SS-304	SS-304

Table 11. Flash drum configurations. Designed with a demister.

Parameter	V-101
Height (m)	3.058
Diameter (m)	0.61

Parameter	V-101
Height (m)	3.058
Head Type	Elliptical
Shell Thickness (in.)	2.057
Head Thickness (in.)	4.68

Table 12. Process conditions for all streams

Parameter	Inlet	1	2	3	4	5	6	7
Temp (°C)	25	200	13	319	466	149	17	-24
Pressure (bar)	1	100	100	99.16	98.2	98.2	98	98
Vapor Fraction	1	1	1	1	1	1	1	1
Flow (ton/h)	2.1	2.1	12.98	12.98	12.98	12.98	12.98	12.98
Flow (kmol/h)	247	247	1,495	1,495	1,495	1,495	1,495	1,495
N ₂ Mol Frac.	0.25	0.25	0.245	0.245	0.222	0.222	0.222	0.222
H ₂ Mol Frac.	0.75	0.75	0.735	0.735	0.667	0.667	0.667	0.667
NH ₃ Mol Frac.	0.0	0.0	0.02	0.02	0.111	0.111	0.111	0.111
Parameter	8	9	10	11	12	13	14	
Temp (°C)	-24	-24	-23	7	107	-45	5.65	
Pressure (bar)	98	98	100	1	0.82	1	0.86	
Vapor Fraction	0	1	1	0	1	1	1	
Flow (ton/h)	2.1	10.9	10.9	30	30	17.4	17.4	
Flow (kmol/h)	124	1,249	1,249	1,665	1,665	1,022	1,022	
N ₂ Mol Frac.	0.0007	0.244	0.244	0.0	0.0	0.0	0.0	
H ₂ Mol Frac.	0.002	0.733	0.733	0.0	0.0	0.0	0.0	
NH ₃ Mol Frac.	99.7	0.023	0.023	0.0	0.0	1.0	1.0	

Table 13. Cost of manufacturing expense breakdown

Direct Manufacturing Costs	
Expense	Cost [\$ per a year]
Cooling Water Required:	140.00
Wind Farm Electricity	1,058,823.53
Chilled Water Required:	–
Low Temperature Refrigerant Required:	32,510.00
Membrane Cost	4,235.29
Ru Catalyst Costs:	821,250.00
Direct supervisory and clerical labor:	170,100.00
Maintenance and repairs:	2,323,510.36
Operating supplies:	348,526.55
Laboratory charges:	141,750.00
Patents and Royalties:	429,639.54
Total	5,330,485.28
Fixed Manufacturing Costs	
Expense	Cost [\$ per a year]
Depreciation:	1,936,258.63
Local Taxes and Insurance:	1,239,205.52
Plant overhead costs:	2,063,166.22
Total	5,238,630.37
General Manufacturing Expenses	
Expense	Cost [\$ per a year]
Administration costs:	515,791.55
Distribution and selling costs:	1,575,344.99
Research and Development:	716,065.91
Total	2,807,202.45
COM	

Expense	Cost [\$ per a year]
COM with Depreciation	14,321,318.10
COM without Depreciation	12,385,059.47

Table 14. Equipment Cost

Hydrogen Synthesis		
Equipment	Bare Module Cost [\$]	Amount
NEL A3880 Electrolyzer	13,622,767	2
Water Purification Unit	150,000	1
Nitrogen Synthesis		
Equipment	Bare Module Cost [\$]	Amount
Compressor (Rotary)	362,000	1
Membrane Frame	12,426	1
Ammonia Synthesis		
Equipment	Bare Module Cost [\$]	Amount
PFR 1 (PBR)	3,210,000	1
Flash Sep	137,000	1
Heat Exchanger 0 (H-201)	292,000	1
Heat Exchanger 1 (H-202)	1,190,000	1
Heat Exchanger 2 (H-203)	570,000	1
Compressor 1 (C-201)	5,190,000	1
Compressor 2 (C-202)	121,000	1
Chiller	260,000	1

Table 15. Depreciation Schedules

MACRS Schedule	BTROI %	DCFROR%	MIRR%	NPV (\$ in millions)
5 year	24.99	14.78	14.75	16.07
7 year	24.99	14.82	14.77	16.36

Table 15. Depreciation Schedules

MACRS Schedule	BTROI %	DCFROR%	MIRR%	NPV (\$ in millions)
5 year	24.99	14.78	14.75	16.07
10 year	24.99	15.60	15.00	17.39

Table 16. Required Operating Labor Cost Estimate

Parameters	Amount
P	0
N _{np}	11
Number of Operators/shift	3
Cost of all operators with salary	\$945,000.00

Table 17. Capital Expenditures

Expenditure	Cost (\$ in millions)
Fixed Capital Investment	38,725,172
Working Capital	2,861,958
Total Capital Investment	41,587,131
Cost Of Manufacturing	12,385,059
BTROI %	24.99
DCFROR%	15.60
MIRR%	15.00
NPV (\$ in millions)	17.39

Appendix C - Example Calculations and Equations

Sample Calculations of Membrane Mass Balance

To find the permeate stream composition, the pressure ratio between the feed and permeate must be found using the following equation:

$$\phi = \frac{P_f}{P_p} = \frac{10 \text{ bar}}{1 \text{ bar}} = 10 \quad (13)$$

Where the feed pressure is $P_f = 10 \text{ bar}$ and $P_p = 1 \text{ bar}$. Once the pressure ratio has been determined, it will then be used to calculate the permeate composition, given that selectivity of the PPO membrane is $\alpha = 4.5$ and the mole fraction of O_2 in the feed is $y_{O_2} = 0.22$:

$$y_{O_2,p} = \frac{10}{2} \left[0.22 + \frac{1}{10} + \frac{1}{4.5 - 1} - \sqrt{\left(0.22 + \frac{1}{10} + \frac{1}{4.5 - 1} \right)^2 - \frac{4(4.5)(0.22)}{10(4.5 - 1)}} \right] \quad (14)$$

$$y_{O_2,p} = 0.510$$

After finding $y_{O_2,p}$, a total mole balance and balances of each species can be performed and expressed in an algebraic expression:

$$\begin{aligned} n_f &= n_p + n_r \\ 0.220n_f &= 0.510n_p + 0.001n_r \\ 0.780n_f &= 0.490n_p + 0.999n_r \end{aligned} \quad (15)$$

Which can then be rearranged to the following expression:

$$\begin{aligned} n_r &= n_f - n_p \\ 0.001n_r &= 0.510n_f - 0.220n_p \\ 0.999n_r &= 0.490n_f - 0.780n_p \end{aligned} \quad (16)$$

From the desired N_2 flow rate of $n_{N_2} = 17.61 \text{ mol/s}$, the mole balance can be used to determine the total retentate molar flow rate of $n_r = 17.62 \text{ mol/s}$. Using these retentate values along with the linear algebra solver in the NumPy library of Python, the flow rates of the permeate and feed streams can be determined as $n_p = 13.32 \text{ mol/s}$ and $n_f = 30.93 \text{ mol/s}$ respectively, thus completing the membrane mass balance.

Sample Calculation of Membrane Sizing

To calculate the size of the membrane, the molar flux of O_2 and molar flow rate of O_2 in the permeate is required, as the area of the membrane can be calculated with the following expression:

$$A_m = \frac{n_{O_2,p}}{j_{O_2,p}} \quad (17)$$

As previously determined, the molar flow rate of the O_2 in the permeate is $n_{O_2,p} = 6.79 \text{ mol/s}$. The permeate flux of the O_2 , however, is directly proportional to the O_2 permeance of the membrane and the pressure difference across the membrane, which can be expressed as the following equation:

$$j_{O_2,p} = Pe_{O_2}(P_{O_2,f} - P_{O_2,p}) \quad (18)$$

Relating this equation to total pressure of the feed and permeate, the equation becomes:

$$j_{O_2,p} = Pe_{O_2}(y_{O_2,f}P_f - y_{O_2,p}P_p) \quad (19)$$

As previously mentioned, the permeance of O_2 with the PPO membrane is $Pe_{O_2} = 200$ GPU, which is equivalent to $Pe_{O_2} = 6.7 \times 10^{-8}$ mol O_2 /m² s. Using the predetermined parameters, the molar flux can be found:

$$j_{O_2,p} = 6.7 \times 10^{-8} \frac{\text{mol } O_2}{\text{m}^2 \text{s}} (0.22 \times 10 \times 10^5 \text{ Pa} - 0.510 \times 1.0 \times 10^5 \text{ Pa})$$

$$j_{O_2,p} = 0.0113 \frac{\text{mol } O_2}{\text{m}^2 \text{s}} \quad (20)$$

Once the flux has been determined, the approximate area of the membrane necessary can be found:

$$A_m = \frac{6.79 \frac{\text{mol } O_2}{\text{s}}}{0.0113 \frac{\text{mol } O_2}{\text{m}^2 \text{s}}} \quad (21)$$

$$A_m = 599.6 \text{ m}^2$$

Flash Separator Sizing

$$H_L = \frac{4t_L Q_L}{\pi D^2} \quad (22)$$

$$L = H_L + H_v \quad (23)$$

$$L = \frac{4t_L Q_L}{\pi D^2} + H_v \quad (24)$$

$$H_v = 4 \text{ ft} \quad (25)$$

$$\frac{L}{D} = 6 \quad (26)$$

A system of equations will be set up with equations 3 and 5 to solve for the unknown height (L) and diameter (D).

$$L = \frac{(16 \text{ min})(0.479094 \text{ ft}^3/\text{min})}{\pi D^2}$$

$$\frac{L}{D} = 6$$

Solving the system of equations yields $L = 9.834$ ft and $D = 1.6539$ ft. A diameter of 2 feet and height of 10 feet suffices the heuristic that the height-diameter ratio is between 2 and 6.

Thickness and Mass of Flash Drum

$$t_{shell} = \frac{PD}{2SE - 1.2P} + t_{ca} \quad (27)$$

$$h = 0.134D \quad (28)$$

$$\rho = 8000 \text{ kg/m}^3 \quad (29)$$

$$P = 100 \text{ bar} \quad (30)$$

$$K = \frac{1}{6} \left(2 + \left(\frac{D}{2h} \right)^2 \right) \quad (31)$$

$$t_{head} = \frac{PDK}{2SE - 0.2P} + t_{ca} \quad (32)$$

$$mass = m_{shell} + m_{head} \quad (33)$$

$$m_{shell} = 1.15D\pi Lt_{shell}\rho \quad (34)$$

$$m_{head} = 1.15 \frac{\pi D^2}{4} \left[1 + \left(\frac{2h}{D} \right)^2 \left(2 - \frac{2h}{D} t_{head} \rho \right) \right] \quad (35)$$

E is welded joint efficiency, S is the Allowable Stress in kPa, and t_{ca} is the corrosion allowance, and the values used in the calculation are for stainless steel 304.

$$t_{shell} = \frac{(100 \text{ bar})(2 \text{ ft})}{2(724 \text{ bar})(1) - (1.2)(100 \text{ bar})} + 0.02 \text{ ft} = 0.17 \text{ ft}$$

$$K = \frac{1}{6} \left[2 + \left(\frac{2 \text{ ft}}{2(0.268 \text{ ft})} \right)^2 \right] = 2.654$$

$$t_{head} = \frac{(100 \text{ bar})(2 \text{ ft})(2.654)}{2(724 \text{ bar})(1) - (0.2)(100 \text{ bar})} + 0.02 \text{ ft} = 0.39 \text{ ft}$$

Economic Equations

$$\log_{10}(C_P^0) = K_1 + K_2 \log_{10}(A) + K_3 [\log_{10}(A)]^2 \quad (36)$$

$$\log_{10}(F_P) = C_1 + C_2 \log_{10}(P) + C_3 [\log_{10}(P)]^2 \quad (37)$$

$$F_T = 1 + 0.00184\Delta T - 3.35 \times 10^{-6}(\Delta T)^2 \quad (38)$$

$$F_{P,vessel} = \frac{1}{t_{min}} \left(\frac{PD}{2SE - 1.2P} + t_{ca} \right) \quad (39)$$

$$\frac{C_A}{C_B} = \frac{I_A}{I_B} \quad (40)$$

$$C_{TM} = 1.18 \sum_{i=1}^n C_{BM,i} \quad (41)$$

$$FCI = C_{GR} = C_{TM} + \frac{1}{2} \sum_{i=1}^n C_{BM,i}^0 \quad (42)$$

$$\text{Number of Operators/Shift} = (6.29 + 31.7P^2 + 0.23N_{NP})^{0.5} \quad (43)$$

$$CF = -fC_{TDC} - WC + (1 - t)(\text{Sales} - COM - D) + D \quad (44)$$

$$DCF = \frac{CF}{(1 + i)^k} \quad (45)$$

$$CCP = (\text{Cumulative Present Value})_{\text{Year } k-1} + \frac{CF_k}{(1 + i)^k} \quad (46)$$

Electrolyzer Costing

The cost of the electrolyzers were estimated using an economies of scale assumption. The scale factor was assumed to be 0.5^[43]. A 1 MW electrolyzer will cost \$1,500,000^[20], so all the information necessary to estimate the cost of a 17.6 MW electrolyzer can be found.

$$\frac{C_{17.6MW}}{C_{1MW}} = \left(\frac{I_{17.6MW}}{I_{1MW}} \right)^n \quad (47)$$

$$C_{17.6MW} = \left(\frac{17.6MW}{1MW} \right)^{0.5} \cdot \$1,500,000 \quad (48)$$

$$C_{17.6MW} = \$6292853.08902$$

This is the cost for one A3880 Electrolyzer so this value would be doubled to yield \$12,585,706.