Letter of Transmittal

May 15th, 2020
To:
Sarah Ewing
AIChE Student Programs
120 Wall Street, FL 23
New York, NY 10005-4020

Dear Managerial Team,

The following report is titled "Industrial Production of Ammonia Fertilizer Using Cyanobacteria." The purpose of writing this report is to submit a preliminary design for an ammonia fertilizer synthesis plant to the 2020 AIChE Student Design Competition. This project was officially started on March 31st, 2020, and is being submitted for approval on May 15th, 2020.

The focus of this report is to explain the preliminary design for an ammonia synthesis plant with a capacity of 50 metric tons per day of anhydrous liquid ammonia, as well as to determine the economic viability of proceeding with the proposed chemical plant design. Additional information is also available in the following report, pertaining to plant safety and other plant considerations.

This is submitted as the final copy of the preliminary design report. Please let us know if you have any questions or concerns. Thank you for your consideration of this preliminary chemical plant design.

Sincerely,
S.H.Y Engineering

Caitlin Hudecek, Robert Schock, and Matthew Young

Modular Production of Anhydrous Ammonia Using Cyanobacteria

AIChE 2019-2020 Student Design Competition

Team 3

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I. Abstract

Today, various types of fertilizers are used to improve crop yields and are integral to sustaining the world's ever-increasing population. Ammonia is a common form of fertilizer that is currently sustaining half of food supply for the world's population, but its production is often energy intensive and heavy in greenhouse gas emissions. The preliminary design of a new ammonia synthesis plant, with a capacity of 50 metric tons per day (mptd), was proposed. It was decided that the main method of ammonia synthesis should be using largescale bioreactors full of ammonia producing cyanobacteria, to reduce the energy requirements and greenhouse gases of the fertilizer plant. The ammonia would then be separated from the liquid medium using membrane technology, again hoping to take advantage of low energy input processes. Finally, the ammonia would be concentrated and liquified using selective absorption technology. Because many of the major proposed unit operations have not been scaled up to industrial sizes or have not been employed in traditional ammonia manufacturing processes, academic studies, opposed to industrial data or correlations, were used as the primary source for sizing and costing the chemical plant. It is also worth noting that it was decided that the plant be extremely modular, operating in 60 parallel paths to attain the desired overall production rate.

The final proposed plant had an installed capital cost of \$461,000,000,000 assuming a Lang factor of 1.7, which is typical for modular plants. Additionally, the proposed plant had an annual operating cost of \$155,710,000,000. The largest component to this operating cost was the capital related costs, which costed \$120,000,000,000 per year. The sales price of the ammonia product, assuming a 25% profit margin, was \$8981.1 per kilogram. This is not competitive on the market today. The profitability metric used to evaluate plant viability was Discounted Cash Flow Rate of Return (DCFROR). The fertilizer plant was found to have a DCFROR of -7.6% over the plants expected 20-year operating lifetime. This plant has been deemed not profitable as it currently stands, and it is not recommended that this plant get built. Instead, further sensitivity analysis into the price of less widely used technology, such as the bioreactor and the medium, be further investigated. Additionally, sensitivity of component cost to bacterial productivity should also be considered. There is the potential that a reasonable increase in bacterial ammonia production rate could result in a much smaller chemical plant, which would also serve to reduce the exorbitant costs of the materials related to the biological processes, which were seen to be the largest source of cost in the system.

II. Introduction

Fertilizer is incredibly important in the world today. Its widespread employment during the Green Revolution in the mid-20th century has drastically increased the yield of crops, allowing more food to be produced in the same area. The increased use of fertilizers has essentially increased food production without changes in the amount of farmable land, which has helped the world to continue producing enough food for an ever-increasing global population. Because of the importance of fertilizers, they have been continually employed in industrial agriculture in recent decades, and their usage only continues to increase as the demand for crops increases with growing global population.

Fertilizers help plants to grow by providing easily accessible nutrients that plants require to grow. The main limiting nutrient for all plants is nitrogen. Plants require nitrogen to effectively photosynthesize because it is a major component in chlorophyll. Chlorophyll is the compound that plants use to convert the energy from sunlight and carbon dioxide into simple sugars, which are then used for energy. If a crop is nitrogen limited, it will have less chlorophyll, reducing the amount of energy it can produce and ultimately stunt the crops growth. Smaller crops mean less food grown by a single plant, which is a problem.

Approximately 79% of Earth's atmosphere is composed of nitrogen gas, which seems to imply that crops should have all the nitrogen they could need. The issue is that nitrogen gas has the chemical formula of N_2, and is composed of two individual nitrogen atoms that are triply bonded to one another. Triple bonds are some of the strongest chemical bonds that are observed and are therefore incredibly difficult to break. Plants require free nitrogen, rather than triply bonded N_2, for use in chlorophyll, but they often to not have the biological processes required to break apart the available nitrogen gas in the air. This means that any useful nitrogen fertilizers require nitrogen in a more accessible state.

The most common chemical used as a nitrogen supplying fertilizer is ammonia. Ammonia, with the chemical formula of NH_3, has nitrogen that is much easier to access than the typical nitrogen gas that is abundant in the air. It lacks triple bonds, instead sporting single bonds between the nitrogen and hydrogens. This means that the nitrogen is much easier to get on its own and is much more readily incorporated into the chlorophyll of the plant. It is worth noting that ammonia, under normal conditions, is a colorless gas. It is often combined with some other chemicals to form a solid salt that is soluble in water, to allow for easier application. It can also be applied directly onto crops but must be pressurized so that it becomes a liquid which can be sprayed over crops and get absorbed into the ground before it vaporizes. Either way, ammonia is used extensively in the production of fertilizers. Some estimates state that the food supply for half of the world's current population is sustained using ammonia fertilizers.

Because ammonia is such an important tool for sustaining food production at levels required to keep the world's population fed, it also has an expectedly large industrial footprint. It is estimated that worldwide, ammonia production uses between 1-3% of the world's total energy consumption. Additionally, it accounts for approximately 5% of natural gas usage and for roughly 3% of the total greenhouse gas emissions. So, just from these above numbers it can be seen that ammonia production has a sizeable impact not only on agricultural processes, but also on the environment.

The traditional process for making ammonia on an industrial scale is the Haber-Bosch process. This reaction scheme was developed over a century ago, in 1910. This process involves reacting pure nitrogen gas with pure hydrogen gas, using some metal catalyst at very high temperatures and pressure. Attaining these operating conditions required for the Haber-Bosch synthesis to occur is energy intensive, and also introduces potential locations for catastrophic failure in the plant.

Because of the necessity for pure feedstocks, ammonia production plants also require the ability to generate their own nitrogen and hydrogen gases. Nitrogen gas is traditionally acquired via the cryogenic distillation of air, which involves cooling the air down enough so that the oxygen in air preferentially liquifies, allowing most of the oxygen to be removed from the remaining purified nitrogen gas due to phase differences. Other methods for producing high quality nitrogen gas include membrane technologies, which depend on differences in gas diffusion rates through a designed thin membrane, or pressure swing adsorption, which uses differences in a solid material's ability to preferentially adsorb or release gases depending on the ambient temperature.

As for the hydrogen production, the most often employed technique is steam methane reformation. Steam methane reformation involves inputting enough energy to a system to cause methane, a major component of natural gas, to react with steam to produce carbon monoxide/carbon dioxide and hydrogen gas. This outlet mixture would then be purified to remove the contaminant gases from the hydrogen gas, often using similar processes as the nitrogen purification schemes. Carbon monoxide and carbon dioxide are vented out into the atmosphere, which accounts for a significant percentage of a plant's greenhouse gas emissions. An alternative method for hydrogen production is the electrolysis of water, which entails running enough electrical current through water to split the water molecules themselves to create oxygen and hydrogen gas. Through electrolysis, the oxygen and hydrogen gases are produced at separate ends of the system, which minimizes the need for separation processes downstream.

As shown in the above paragraphs, traditional synthetic ammonia production requires a lot of effort. It is energy intensive, is heavily dependent on largely non-renewable feedstocks such as natural gas and produces a significant amount of greenhouse gases which contribute to the issue of human-driven climate change. But, this process of "fixing" nitrogen from its gaseous state to an ammonia form usable by plants occurs naturally! Plants grew before the human invention of ammonia fertilizers, so there must be some alternative method to produce ammonia which would reduce the environmental impacts of traditional ammonia production.

It has been determined that there are numerous types of bacteria that can "fix" nitrogen that live symbiotically with plants. While the plants do not have the biological hardware to change atmospheric nitrogen into the nitrogen they need to grow, they have developed relationships with microbes that can. These bacteria only require nitrogen from the air, water, and some carbon source to grow and produce the usable nitrogen that plants require to effectively grow. It stands to reason that it is possible to produce ammonia with low energy requirements and low greenhouse gas emissions harnessing the power of these micro-organisms in bioreactors.

Various experimental studies have demonstrated that it is possible to generate noticeable levels of ammonia doing just that. By cultivating specialized strains of cyanobacteria, researchers have continually been able to produce small amounts of ammonia, only needing to supply the microbes with food and air.[53,55] The success has been promising, but it is worth noting that most of these processes have not been scaled up to industrial scales. But, given the small-scale success of this ammonia generation using photobioreactors, it seems like a viable avenue for industrial level ammonia production. Additionally, since photobioreactors generally come in relatively small sizes compared to the average area of industrial production facilities, it would be incredibly easy to make the proposed plant highly modular. Further information about the individual research studies can be found in the appendix, under photobioreactor design below.

The use of membranes is an attractive method for removing dilute ammonia from a liquid medium, making it worth exploring. Membrane technology has been used to remove ammonia from water on somewhat large scales, often finding use in wastewater treatment facilities. So, it is known that membranes can be used to remove dilute ammonia from liquid water at some sense of economical scale, which is already a benefit. The issue is that because it is used in wastewater applications, the clean water is the product and the ammonia is a contaminant to be removed and discarded, making it difficult to find industrial data on the exact efficacy of utilizing scaled up membranes to produce ammonia. However, there are multiple lab studies that study membrane removal of ammonia from water, looking at ammonia as the product, giving useful data for membrane design.[39] The result is that the ammonia will be preferentially removed from the liquid medium and be transferred to a gaseous air stream for purification downstream. Elaborations on these studies can be found in the material and energy balances section for the membrane below.

Finally, the final major unit operation to discuss is the purification of the gaseous air stream mixed with the desired ammonia product. To effectively separate the ammonia from the air, selective absorption will be employed. As stated earlier, this depends on the preferential absorption of one gas species into a porous solid media at high pressure. The vessel is then vented, pulling out one gas while the other gas remains adsorbed onto the solid material. Once the waste gas is vented and the solid material becomes saturated with the desired gas species, which is ammonia in this case, the pressure is lowered and the temperature is increased so that the ammonia desorbs off of the solid media, resulting in a very pure outlet stream of ammonia. As with the previous unit operations discussed, there are very few instances of the technology being employed for this exact purpose, but there are examples of it being used in similar enough processes that it is expected to work in this instance. Additionally, smaller scale studies were found confirming these suspicions, which can be found in greater detail in the material and energy balances section for the purification stage below.[25]

III. Process Description

Photobioreactors

The photobioreactor is responsible for the cultivation of the cyanobacteria *Anabaena siamensis* which are being used to create the ammonia for the plant. These specific cyanobacteria were chosen because of their ammonia production rates and because of the detail of their properties and culture in the study by Thomas et al.[46] The photobioreactor (PBR) consists of clear, 25 ft PVC pipes (6" diameter) oriented vertically and connected in series in a winding pattern. B-11 cell culture medium (supplemented to pH of ~9.4 with NaOH) and cyanobacteria are flown through the photobioreactor at 27.6 m^3/s. Aeration (with air containing 1.5% CO_2) and thus mixing occur every 10 tubes via a sparger at the bottom of the tube at a flow rate of $6.95 *10^{-3}$ m^3/s. The PBR is contained in a greenhouse for easier temperature control and maintenance, with rows of the connected PVC tubes being 3ft apart. Every other row has flat LED lights for supplemental lighting during periods of insufficient light (winter, clouds, etc). A pump below the sparger helps to keep flow going to subsequent tubes. A 3 inch separation between vertical pipes was assumed and 10% excess in volume was added for assurance in producing 50 metric tons per day of anhydrous ammonia, meaning that $2.4*10^6$ L of medium were needed and a space of 1121 acres required.

A. siamensis has a doubling time of 5.6 hours and at the start of the PBR is introduced at a concentration of 6 µg chlorophyll mL^{-1}.[46] Since the cyanobacteria were observed to produce the most ammonia when the population density is between 5-7 µg chlorophyll mL^{-1}, cyanobacteria is removed from the system at 18 different points along the PBR.[46] At these points of removal, part of the feed is removed from the system and sent to a continuous centrifuge that spins out all of the cyanobacteria. The removed cyanobacteria are considered waste and the cyanobacteria-free liquid is sent over a membrane to remove the ammonia. The liquid is reintroduced back into the photobioreactor right after it was removed to keep the total volumetric flow rate constant through the PBR. Although the membrane works best at higher temperatures, it was decided to not include heat exchangers here to heat up the liquid before the membrane and then cool it back down after the membrane because of the energy costs and the fact that ammonia removal at these areas is not vital. These diversions of flow occur in the process when the concentration reaches the maximum 7 µg chlorophyll mL^{-1}. After the removal the concentration inside the PBR is reset to 6 µg chlorophyll mL^{-1}. The starting concentration was chosen to be 6 µg chlorophyll mL^{-1} because that concentration allows for higher amounts of ammonia being produced per liter but also limits the number of centrifuges needed in the system. The removal of the ammonia as well as the excess cyanobacteria helps to prevent the inhibition of ammonia production within the PBR. At the end of the photobioreactor system the entire flow is directed to the membrane system.

Membrane

The bioreactor effluent must be treated to effectively remove the ammonia that the cyanobacteria generated. Firstly, the effluent stream needs to be split and centrifuged. The stream is split in such a way that the cyanobacteria centrifuged from one stream is the amount required to maintain the desired cell concentration for optimal bioreactor performance. These cyanobacteria are reintroduced to the bioreactor liquid at a later stage. The other centrifuge removes all other cyanobacteria, and sends them out as waste.

It is important that the cyanobacteria are removed from the liquid at this moment, because the temperature of solution needs to get raised to a level that would be detrimental to the cyanobacteria to get higher mass transfer across the membrane apparatus. So, the bioreactor effluent, now devoid of cyanobacteria, is sent through a heat exchanger where it is heated from 42 °C to a temperature of 80 °C for higher ammonia mass flux through the membrane. The bioreactor effluent is then run through the membrane system, where low pressure air serves as a sweep gas to preferentially remove the ammonia from the liquid stream. The sweep gas leaves, now rich in ammonia, and is sent downstream for purification.

The remaining liquid is then sent through another heat exchanger, where it is cooled back down to 42 °C. A small amount of cell medium is pulled away from the system, while the rest of the cell medium is sent to a large mixed tank where the cyanobacteria pulled off earlier in the centrifuge are reintroduced to the medium. In this tank, some new cell medium is pumped in, to replace the old medium that was being pulled off. It was assumed that the plant would add 5% of its total volume of liquid every week, to ensure the cyanobacteria is not starved of nutrients. This mix of cyanobacteria and liquid feed are then ready to get pumped back into the system, to go through the photobioreactor once again.

Purification

After removing the ammonia from the water in the membrane, it must be separated from the low-pressure air permeate. Selective absorption is used to purify the 1.7 mol% ammonia into anhydrous ammonia. The permeate feed is compressed to 1.5 bar and cooled to 200 °C through a 20 MW compressor and shell and tube heat exchanger, with 20 °C cooling water, respectively. A 40 wt% $MgCl_2$ and 60 wt% silica gel acts the solid absorbent that selectively absorbs ammonia. Under the 200 °C, 1.5 bar absorption operating conditions, the air and remaining water does not have a tendency to absorb into the absorbent. Thus, as the mixture flows through the packed bed of absorbent, 99.5% of the ammonia is absorbed, and the rest of the mixture is recycled to the permeate after a vacuum pump returns its pressure to 17.3 kPa. To desorb the ammonia from the temperature of the packed absorbent bed is increased to 392 °C via inductive heating coils in a jacket around the vessel. The pressure is also lowered to 1 bar by opening the ammonia outlet of the vessel, which allows the purified ammonia to evacuate the system. The absorber cycle has 4 key steps (it is not continuous): absorption, heating, desorption, and then cooling back to absorption conditions. It was designed such that each step took the same amount of time. With this, there are 4 absorbers per module, with each one at a different stage in the cycle to ensure the system approaches a continuous process. After desorption, the 99.6 wt% ammonia product (some water was assumed to have remained in the system despite it being above absorption conditions for water) is pre-cooled to 50 °C via 12.7 kmol/hr of 20 °C cooling water in a shell and tube heat exchanger. The product is then compressed to 200 psia by a 7.1 kW compressor and condensed/cooled to 30 °C via 90.4 kmol/hr of 20 °C cooling water in a shell and tube heat exchanger. Finally, the liquid anhydrous ammonia product is sent to storage tanks. The same process occurs for each module, however single-module flows and energy requirements were provided here. All heat exchangers operated in a counter-current configuration to maximize the temperature driving force. A more detailed discussion is available in Section VI.

IV. Process Flow Diagrams

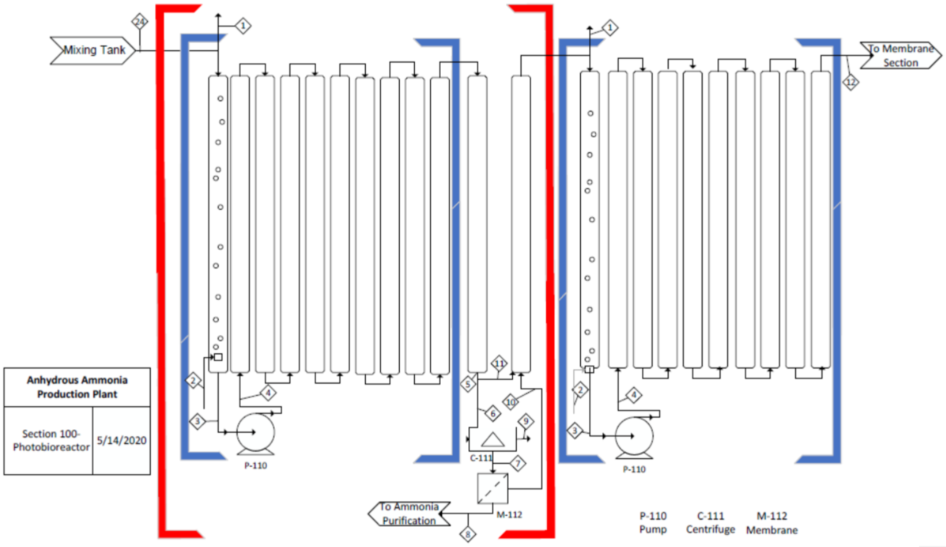


Figure 4.1: The Photobioreactor. The aeration/pump repeating units are indicated by the blue brackets. Aeration occurs every 10 pipes, and then a pump sends the fluids through to the next aeration pipe. This unit is repeated 1504 times per centrifuge unit and 1504 times after the last centrifuge unit. The centrifuge repeating units are indicated by the red brackets and include the aeration/pump repeating units. Per module, the centrifuge repeating unit is repeated 18 times.

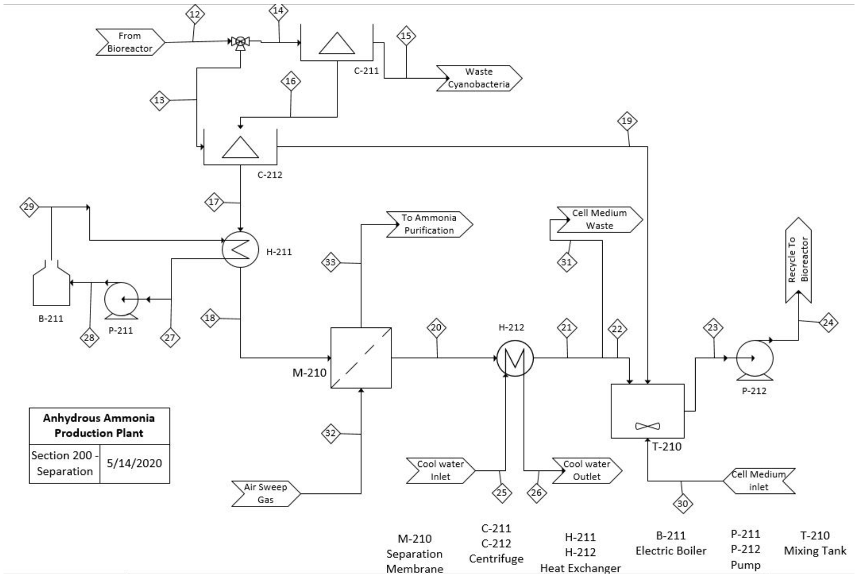


Figure 4.2: The Separation System. The system above is designed to remove the ammonia produced by the cyanobacteria from the liquid cell medium. A membrane is the primary driver of this separation, with the cell medium flowing through a membrane system while low pressure air is sent across the other side of the membrane as a sweep gas. Before being sent to the membrane, the cyanobacteria are removed from the system and then the cell medium has its temperature increased. After running through the membrane, the cell medium is cooled off to temperatures suitable for the cyanobacteria, a small portion of the cell medium is removed from the system, and then the cyanobacteria are reintroduced into the system with enough new medium to balance what was lost. These streams are all mixed together, and then recycled through the bioreactor system.

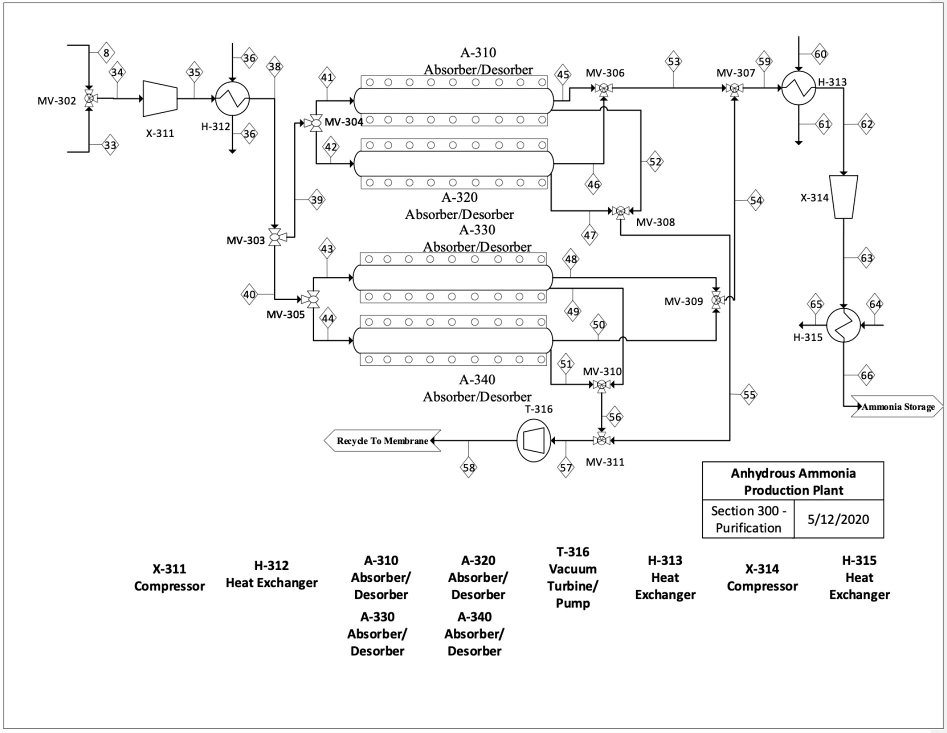


Figure 4.3: The Purification System. The air/ammonia mixture from the membrane permeate is first compressed to 1.5 bar, then cooled to absorption conditions at 200 °C. There are 4 absorbers, which follow a staggered cycle of absorption, heating, desorption, and cooling. The staggering allows the process to be continuous. The ammonia is selectively absorbed by a magnesium chloride/silica gel solid absorbent, and the air is recycled back to the membrane. The ammonia desorbs at 392 °C and 1 bar, and is then compressed to 200 psia and condensed to a liquid for storage and transportation.

V. Assumptions & Nomenclature

Assumptions

- Adiabatic Compression
- Compressor efficiency of 75%
- Turbine efficiency of 75%
- Lang factor of 1.7
- Learning rate of 20% ($p = 0.8$)
- Absorbent void fraction of 0.4
- Minnesota wind energy capacity factor of 36%
- Corporate tax rate of 21%

- Interest rate of 8%
- 10 kPa pressure drop for liquids through shell & tube heat exchanger
- Negligible pressure drop for gases through shell & tube HX
- Negligible pressure drop for all fluids through piping
- Non-ideal gas and liquid behavior
- Countercurrent heat exchangers
- Air is 79 mol% nitrogen, 21 mol% oxygen
- Yearly labor-related costs are 60% of yearly operating labor costs
- Yearly capital-related expenses are 26% of the initial CAPEX
- Oct. 2019 CEPCI of 599.5 is a sufficient estimate for 2020 costs
- Profit margin of 25%
- Sales related costs are 20% of yearly sales
- 20-year effective plant life
- 5-year MACRS schedule over 20-year period
- Aeration in the photobioreactor is enough to disrupt the flow completely
- Culture medium in the photobioreactor has properties of water
- *Anabaena siemensis* follows an exponential population growth model
- Energy storage requirements are 2/3 of total energy requirements

Nomenclature

Symbol	*Name*	*Units*
$\mathbf{P}$	Pressure	kPa or psi
$\mathbf{T}$	Temperature	K or °C
$\dot{n}$	Molar flow rate	kmol/hr
A	Area	m^2
r_{abs}	Rate of absorption	mol NH_3/kg_{abs}-s
r_{des}	Rate of desorption	mol NH_3/kg_{abs}-s
ΔH_{abs}	Enthalpy of absorption	J/mol
k_{abs}	Absorption rate constant	mol NH_3/(kg_{abs}-bar-s)
K_{abs}	Absorption rate fitting parameter	bar^6
k_{des}	Desorption rate constant	mol NH_3/(kg_{abs}-bar-s)
R	Gas constant	J/mol-K
V	Volume	m^3
m	Mass	kg
ρ	Density	kg/m^3
σ_{hoop}	Hoop stress wall thickness	m
$\sigma_{longitudinal}$	Longitudinal stress wall thickness	m
D	Diameter	m
S	Maximum allowable stress	ksi
E	Weld efficiency	Dimensionless
KE	Kinetic energy	J
v	Velocity	m/s

t	Time	Seconds
J	Power output	kW
C	Power efficiency coefficient	Dimensionless
x	Liquid mole fraction	Dimensionless
y	Vapor mole fraction	Dimensionless
PBR	Photobioreactor	-
vvm	Volume air per volume liquid per minute	min^{-1}
TEMA	Tubular Exchangers Manufacturers Association	-

VI. Material & Energy Balances

Material & Energy Stream Tables

Table 6.1. Stream table from describing the temperature, pressure, flowrate, and thermal condition of all streams in the process flow diagram. Flowrates are on a per module molar basis.

Photobioreactor Section				
Stream Number	**Temperature (°C)**	**Pressure (kPa)**	**Flowrate (L/hr)**	**Thermal Condition**
1	**42**	**101**	**$4.17*10^4$**	Subcooled liquid
2	**42**	**101**	**$4.17*10^4$**	Subcooled liquid
3	**42**	**101**	**0.803**	Subcooled liquid
4	**42**	**101**	**$1.66*10^6$**	Subcooled liquid
5	**42**	**101**	**$1.66*10^6$**	Subcooled liquid
6	**42**	**101**	**$2.36*10^5$**	Subcooled liquid
7	**42**	**101**	**$2.36*10^5$**	Subcooled liquid
8	**42**	**101**	**90.9 (g/hr)**	Subcooled liquid
9	**42**	**101**	**1.66 (kg/hr)**	Subcooled liquid
10	**42**	**101**	**$2.36*10^5$**	Subcooled liquid
11	**42**	**101**	**$1.65*10^6$**	Subcooled liquid
Separation Section				
Stream Number	**Temperature (°C)**	**Pressure (kPa)**	**Flowrate (kmol/hr)**	**Thermal condition**
12	**42**	**101**	**91853.5**	Subcooled liquid
13	**42**	**101**	**75496.0**	Subcooled liquid
14	**42**	**101**	**16357.5**	Subcooled liquid
15	**42**	**101**	**2.15 (kg/hr)**	Subcooled liquid
16	**42**	**101**	**16357.5**	Subcooled liquid
17	**42**	**101**	**91853.5**	Subcooled liquid
18	**89**	**101**	**91853.5**	Subcooled liquid
19	**42**	**101**	**9.93 (kg/hr)**	Subcooled liquid
20	**80**	**101**	**91850.9**	Subcooled liquid
21	**42**	**101**	**91850.9**	Subcooled liquid

22	**42**	**101**	**91194.9**	Subcooled liquid
23	**42**	**101**	**91850.9**	Subcooled liquid
24	**42**	**101**	**91850.9**	Subcooled liquid
25	**30**	**101**	**349000**	Subcooled liquid
26	**40**	**101**	**349000**	Subcooled liquid
27	**242**	**3490**	**8374**	Subcooled liquid
28	**242**	**3500**	**8374**	Saturated liquid
29	**242**	**3500**	**8374**	Saturated vapor
30	**42**	**101**	**656.1**	Subcooled liquid
31	**42**	**101**	**656.1**	Subcooled liquid
32	**20**	**17.33**	**118**	Superheated vapor
33	**20**	**17.33**	**120.2**	Superheated vapor
Purification & Recovery Section				
Stream Number	**Temperature (℃)**	**Pressure (kPa)**	**Flowrate (kmol/hr)**	**Thermal condition**
34	**40.1**	**17.33**	**120.2**	Superheated vapor
35	**377**	**150**	**120.2**	Superheated vapor
36	**20**	**101**	**289.5**	Subcooled liquid
37	**50**	**101**	**289.5**	Subcooled liquid
38	**200**	**150**	**120.2**	Superheated vapor
39	**200**	**150**	**60.1**	Superheated vapor
40	**200**	**150**	**60.1**	Superheated vapor
41	**200**	**150**	**30.05**	Superheated vapor
42	**200**	**150**	**30.05**	Superheated vapor
43	**200**	**150**	**30.05**	Superheated vapor
44	**200**	**150**	**30.05**	Superheated vapor
45	**392**	**100**	**0.51**	Superheated vapor
46	**392**	**100**	**0.51**	Superheated vapor
47	**200**	**150**	**29.5**	Superheated vapor
48	**392**	**100**	**0.51**	Superheated vapor
49	**200**	**150**	**29.5**	Superheated vapor
50	**392**	**100**	**0.51**	Superheated vapor
51	**200**	**150**	**29.5**	Superheated vapor
52	**200**	**150**	**29.5**	Superheated vapor
53	**392**	**100**	**1.02**	Superheated vapor
54	**392**	**100**	**1.02**	Superheated vapor
55	**200**	**150**	**59.0**	Superheated vapor
56	**200**	**150**	**59.0**	Superheated vapor
57	**200**	**150**	**118**	Superheated vapor
58	**39.2**	**150**	**118**	Superheated vapor
59	**392**	**100**	**2.04**	Superheated vapor
60	**20**	**101**	**12.7**	Subcooled liquid
61	**50**	**101**	**12.7**	Subcooled liquid
62	**50**	**100**	**2.04**	Superheated vapor
63	**361**	**100**	**2.04**	Superheated vapor

64	**20**	**101**	**90.4**	Subcooled liquid
65	**30**	**101**	**90.4**	Subcooled liquid
66	**30**	**100**	**2.04**	Subcooled liquid

Table 6.2. Mole fraction basis compositions for each stream in the separations and purification sections from the process flow diagram. The photobioreactor section was left out because the repeating units in the PFD meant that there was not just one mole fraction for any given stream.

Separations Section					
	12	**13**	**14**	**15**	**16**
Ammonia (NH_3)	0.000025	0.000025	0.000025	-	0.000025
Water (H_2O)	0.999975	0.999975	0.999975	-	0.999975
Nitrogen (N_2)	-	-	-	-	-
Oxygen (O_2)	-	-	-	-	-
Cell Conc. (g/m^3)	7.3	7.3	7.3		-
	17	**18**	**19**	**20**	**21**
Ammonia (NH_3)	0.000025	0.000025	-	$1.2*10^{-6}$	$1.2*10^{-6}$
Water (H_2O)	0.999975	0.999975	-	~1.000	~1.000
Nitrogen (N_2)	-	-	-	-	-
Oxygen (O_2)	-	-	-	-	-
Cell Conc. (g/m^3)	-	-		-	-
	22	**23**	**24**	**25**	**26**
Ammonia (NH_3)	$1.2*10^{-6}$	$1.2*10^{-6}$	$1.2*10^{-6}$	-	-
Water (H_2O)	~1.000	~1.000	~1.000	1.000	1.000
Nitrogen (N_2)				-	-
Oxygen (O_2)				-	-
Cell Conc. (g/m^3)	-	6.0	6.0	-	-
	27	**28**	**29**	**30**	**31**
Ammonia (NH_3)	-	-	-	-	$1.2*10^{-6}$
Water (H_2O)	1.000	1.000	1.000	1.000	~1.000
Nitrogen (N_2)	-	-	-	-	-
Oxygen (O_2)	-	-	-	-	-
	32	**33**			
Ammonia (NH_3)	-	0.017			
Water (H_2O)	-	0.003			
Nitrogen (N_2)	0.79	0.774			
Oxygen (O_2)	0.21	0.206			
Purification Section					
Component	**34**	**35**	**36**	**37**	**38**
Ammonia (NH_3)	0.0171	0.0171	-	-	0.0171
Water (H_2O)	0.0034	0.0034	1.000	1.000	0.0034
Nitrogen (N_2)	0.7738	0.7738	-	-	0.7738
Oxygen (O_2)	0.2057	0.2057	-	-	0.2057
	39	**40**	**41**	**42**	**43**
Ammonia (NH_3)	0.0171	0.0171	0.0171	0.0171	0.0171
Water (H_2O)	0.0034	0.0034	0.0034	0.0034	0.0034

Nitrogen (N_2)	0.7738	0.7738	0.7738	0.7738	0.7738
Oxygen (O_2)	0.2057	0.2057	0.2057	0.2057	0.2057
	44	**45**	**46**	**47**	**48**
Ammonia (NH_3)	0.0171	0.9962	0.9962	0.00001	0.9962
Water (H_2O)	0.0034	0.0038	0.0038	0.0038	0.0038
Nitrogen (N_2)	0.7738	-	-	0.2092	-
Oxygen (O_2)	0.2057	-	-	0.7870	-
	49	**50**	**51**	**52**	**53**
Ammonia (NH_3)	0.00001	0.9962	0.00001	0.00001	0.9962
Water (H_2O)	0.0038	0.0038	0.0038	0.0038	0.0038
Nitrogen (N_2)	0.2092	-	0.2092	0.2092	-
Oxygen (O_2)	0.7870	-	0.7870	0.7870	-
	54	**55**	**56**	**57**	**58**
Ammonia (NH_3)	0.9962	0.00001	0.00001	0.00001	0.00001
Water (H_2O)	0.0038	0.0038	0.0038	0.0038	0.0038
Nitrogen (N_2)	-	0.2092	0.2092	0.2092	0.2092
Oxygen (O_2)	-	0.7870	0.7870	0.7870	0.7870
	59	**60**	**61**	**62**	**63**
Ammonia (NH_3)	0.9962	-	-	0.9962	0.9962
Water (H_2O)	0.0038	1.000	1.000	0.0038	0.0038
Nitrogen (N_2)	-	-	-	-	-
Oxygen (O_2)	-	-	-	-	-
	64	**65**	**66**		
Ammonia (NH_3)	-	-	0.9962		
Water (H_2O)	1.000	1.000	0.0038		
Nitrogen (N_2)	-	-	-		
Oxygen (O_2)	-	-	-		

Photobioreactors

First, we wanted to figure out the optimal starting population of cyanobacteria in the photobioreactor. Because the cells produce the maximal amount of ammonia in cell densities between 5-7 µg chloroplast/mL, when the concentration reached 7 µg chloroplast/mL cyanobacteria would need to be removed from the system via centrifuges. The optimal system would have a minimal amount of centrifuges and create the most ammonia. In order to find the time it would take to reach the max population density from a given starting point, the exponential growth rate equation was used:

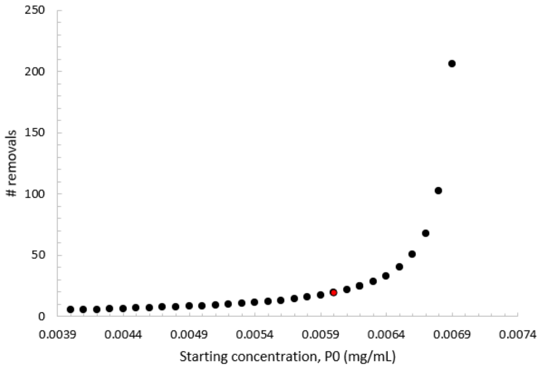
$$P(t) = P_0 e^{0.1238t}$$

Where t=time (hrs) and P=population($\frac{mg\ chloro}{mL}$)

Using excel and this equation, starting concentrations between 5-7 µg chloroplast/mL were tested in 0.1µg chloroplast/mL increments and the time at which the population reached the max was recorded. To find how many times cyanobacteria would have to be removed from the system and reset to the starting population (assuming the entire volume of the plant is cycled in one day):

$$\frac{24hr}{t_{to\ reach\ max}} = \#\ times\ for\ removal$$

From this information, a graph of removals vs starting concentration was made:



From this graph it was determined that a starting concentration of 6 µg chloroplast/mL was optimal because it still started at a higher concentration so more ammonia would be made per unit time but did not require a lot of removal processes. This starting concentration correlated with removal happening 19 times with the time between removals being 1.2 hours.

To model ammonia buildup, an equation based off exponential population growth and experimental ammonia production data from the Thomas, Zaritsky, and Boussiba paper[46] was made to find ammonia at a given time in the PBR:

$$NH_4(t) = 8.7\left(\frac{\mu mol\ NH_3}{mg\ chloro - hr}\right) * P_0 e^{0.1238t}\left(\frac{mg\ chloro}{mL}\right)$$

This model was then integrated in order to find the accumulation of ammonia:

$$NH_3 = 70.29 * P_0 e^{0.1238t} = \left[\frac{\mu mol\ NH_3}{mL}\right]$$

This integrated form was used with the starting concentration of 6 µg chloroplast/mL and a t=1.2 hours to find that the amount of ammonia created was 0.07 µmol/mL. This number was multiplied by the number of removals to find the total amount of ammonia created in a 24 hr time to be 1.35 µmol/mL.

In order to find the required volume needed from our 50mtpd requirement:

$$\frac{5 * 10^7\ \frac{g}{day}}{0.00135\,\frac{mol\ NH_3}{L\ day} * 17.031\,\frac{g\ NH_3}{mol\ NH_3}} = 2.2 * 10^9 L$$

Because of the uncertainties in the ammonia removal, cyanobacteria centrifuge efficiency, and cyanobacteria culture, 10% was added to the volume to give a final plant volume of 2.38*10^9 L. It was decided that the entire plant would cycle through the full volume in one day, so the flow rate was 2.38*10^9 L/day. This is a very fast flow rate, so module sizes of 10, 25, and 60 were looked at in order to determine what would lead to the most realistic flow rate in terms of sizing and flow requirements. 60 modules decreased the flow rate to 3.97*10^7 L/day, and because that was still a high flow rate but more modules than that seemed unreasonable, 60 was chosen for amount of independent modules that plant would be broken down into.

To find the amount of cyanobacteria that needed to be removed every 1.2 hours per module, the flow rates and molarity equation were used:

$$M_1V_1 = M_2V_2$$

$$7\frac{ug\ chloro}{mL} * V_1 = 6\frac{ug\ chloro}{mL} * 1.66 * 10^6\frac{L}{day}$$

Where V_2=total flow rate per module, M_1= max cyanobacteria concentration, M_2= starting cyanobacteria concentration

To find the volumetric flow rate of cyanobacteria needed to be removed:

$$V_2 - V_1 = V$$

Where V is the flow rate needed to be cleared of cyanobacteria.

To determine the volumetric flow rate at the bottom of an aerated pipe, it was assumed that the aeration made the pressure at the bottom of the pipe atmospheric and that the aeration deterred the flow enough so that the flow at the bottom was just due to gravity. Using the Bernoulli equation the flow rate was found:

$$P_1 + \rho g h_1 + \frac{1}{2}\rho v_1^2 = P_2 + \rho g h_2 + \frac{1}{2}\rho v_2^2$$

Where P=pressure, ρ=density, g=gravity, h=height, v=velocity.

If 1 is the top of the pipe and 2 is the flowrate at the bottom, then the equation simplifies to:

$$v_2 = \sqrt{2gh_1}$$

$$v_2 = \sqrt{2 * 9.81\left(\frac{m}{s^2}\right) * 7.62\ m} = 12.3\ \text{m/s}$$

Therefore volumetric flow rate, Q:

$$Q = v_2 * A_{pipe}$$

$$Q = 12.3\frac{m}{s} * 0.0182\ m^2 = 0.223\frac{m^3}{s} = \frac{0.803L}{hr}$$

To determine the power requirement of the pump used to pump the solution after it had been aerated in a pipe, the head loss from fittings and friction and static head were taken into account:

$$h_{static} = (\#pipes\ per\ pump - 1) * pipe\ length$$

$$h_{fitting} = \frac{k * (\#\ 90°\ bends) * v^2}{2g}$$

$$h_f = \frac{f_D * L * v^2}{2 * D * g}$$

Where k=resistant coefficient, v=velocity (m/s), g=gravity (m/s^2), $h_{fitting}$=head loss due to fittings/bends, h_{static}=static head loss, h_f=head loss from friction, f_D=friction coefficient (calculated using Darcy friction factor method), L=total length of 10 pipes (m), D=pipe diameter (m).

Using these methods, the total head (sum of all the heads): H=520m

To find the power, the following equation was used:

$$P = \frac{Q\rho g H}{3.6 * 10^6 * \eta}\ kW$$

Where P=power (kW), Q=volumetric flow rate (m^3/s), ρ=density of fluid (kg/m^3), H=total head (m), and η= efficiency (0.7)

Overall the power per pump was 3MW.

Membrane

Multiple options were explored to determine a reliable way to remove the ammonia product from the cell culture. Originally, a liquid stripping column was proposed, which would run air through the system to preferentially evaporate ammonia from the liquid phase, and transport it into a gas to send to further processing. This ended up not being viable, due to two issues. Firstly, the stripping air would also absorb large amounts of water from the cell culture. This was problematic because since the ammonia was in such low concentrations, the outlet air stream from the column would have a much higher mole percentage of water rather than ammonia. This would place too much pressure on downstream operations to purify the ammonia product. The second, and more glaring issue, was that the air flow for the stripping column was incredibly high. The required air flow rate was so large that it would almost certainly flood the column at any reasonable air velocity, making sizing the column difficult.

Because the stripping column had so many issues, a different form of separation was examined. Membrane separation seemed like a good option, for multiple reasons. Firstly, it is a passive separation process, so there would be very little energy costs associated with running this unit operation. Additionally, membrane separation has been shown to work effectively, even with relatively low ammonia concentrations like what is expected in the outlet stream from the bioreactors. Additionally, by avoiding any form of column, both of the negatives of the stripping column were avoided. There would no longer be any risk of flooding, and by using the right membrane the ammonia would be preferentially absorbed into the sweep gas, making downstream purification steps easier.

Generally, when membranes are employed to remove ammonia from a liquid stream, they are implemented in wastewater treatment plants, where the ammonia is considered a contaminant and is removed from the system. As such, there are very few examples of largescale membrane technologies looking to concentrate ammonia species, making definitive sizing and costing of this unit operation exceptionally difficult. However, there were multiple lab studies done on a small scale, which proved this proof of concept. One study, which was carried out by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Victoria, Australia proved exceptionally useful.[39]

This study analyzed the mass flux of ammonia through a membrane at varying environmental conditions. The feed temperature, sweep gas flow rate, and sweep gas pressure were all varied throughout this study, and provided membrane selectivity and ammonia flux data points for these different sets of experimental conditions. This study also saw a removal efficiency of up to 95%, which is what was used in future sizing calculations. So, using the data from this paper, a rough estimate for achievable ammonia mass flux and selectivity were determined, which also set some fundamental stream properties such as feed temperature and sweep gas flow rate. These experiments were performed on a small scale, with a feed flow rate of just 0.3 L/min and a sweep gas flow rate of 3.0 L/min, but it was assumed that these values would be able to scale up to a larger process. It was determined that a feed temperature of 80 °C, a feed pH of 9.4, a sweep gas pressure of 130 torr, and a sweep gas flow rate of 10 times the feed flow would result in an ammonia flux of approximately 16 grams of ammonia per hour per meter squared (16 g/m^2-hr), and a selectivity of approximately 5.[39] These were the values used to size the membrane unit operation.

The volumetric flow rate from the bioreactor into the membrane section was converted to a usable molar flow rate. The molecular weight of the bioreactor fluid was assumed to be that of water because the mixture is predominantly water with dilute ammonia, cell medium, and cyanobacteria. The density of the solution was also assumed to be roughly that of water for the same reason.

$$n_{12} = 2383488\frac{m^3}{day} * \frac{1\,day}{24\,hr} * \frac{1000\,kg}{1\,m^3} * \frac{1\,kgmol}{18.02\,kg} * \frac{1}{60\,modules} = 91853.5\frac{kgmol}{hr*module}$$

It is also important to calculate the mole fraction of ammonia in this bioreactor feed stream. It was calculated earlier that the cyanobacteria should produce ammonia at a rate of approximately 2.26 kgmol ammonia/hr for each module. This value was then used to calculate the molar composition.

$$x_{NH_3,12} = \frac{\left(2.26\frac{kgmol}{hr}\right)}{91853.5\frac{kgmol}{hr}} = 0.0025\%\ NH_3$$

$$x_{H_2O,12} = 100 - 0.0025 = 99.9975\%\ H_2O$$

The point of using centrifuges C-211 and C-212 are to remove cyanobacteria to get the concentration down to levels that result in optimum growth rate. It was previously calculated that the desired recycle concentration will be 6.0 g bacteria/m^3 solution, and it was also calculated that the cell medium has cell concentration of 7.3 g bacteria/m^3 in stream 12. Therefore, it is necessary to divide the flow proportionally, according to the dilution equation, to remove enough cells. Therefore, stream 14 needs a ratio (7.3-6.0)/(7.3) of the flow from stream 12. The balance then goes to stream 13. The concentrations of these inlet streams do not change at all, as it is only a passive separation process.

$$n_{14} = n_{12} * \frac{1.3\frac{g}{m^3}}{7.3\frac{g}{m^3}} = 91853.5\frac{kgmol}{hr*module} * \frac{1.3}{7.3} = 16357\frac{kgmol}{hr*module}$$

$$n_{13} = n_{12} - n_{14} = 91853.5\frac{kgmol}{hr} - 16357.5\frac{kgmol}{hr} = 75496\frac{kgmol}{hr}$$

To calculate the average flow rate of stream 15, another mass balance was employed. The volumetric flow through C-211 can be calculated, and the concentration of the cyanobacteria is also known. Assuming the centrifuge removes all of the cyanobacteria present in stream 14, the flow rate of stream 15 can be calculated.

$$m_{15} = V_{14} * C_{bact.\ 14} = \frac{1.3}{7.3} * \frac{2383488\,m^3}{day} * \frac{1}{60\,modules} * \frac{day}{24\,hr} * 7.3\frac{g}{m^3} = 2.15\frac{kg}{hr}$$

The flow rate and composition through stream 16 should be the same as through stream 14, except for without the cyanobacteria.

The flow rate through stream 17 should be the sums of the liquid flow rates through streams 13 and 16, using a mass balance. Also, the concentration of the solution with respect to ammonia and water will not change, since the only separation processes involved have Additionally, assuming the centrifuge fully removes all cyanobacteria from the liquid, and removes no other liquid from the system, the mass flow rate of stream 19 can also be calculated.

$$n_{17} = n_{13} + n_{16} = 16357 \frac{kgmol}{hr*module} + 75496 \frac{kgmol}{hr*module} = 91853.5 \frac{kgmol}{hr*module}$$

$$m_{19} = V_{13} * C_{bact.\ 13} = \frac{6}{7.3} * \frac{2383488\ m^3}{day} * \frac{1}{60\ modules} * \frac{day}{24\ hr} * 7.3 \frac{g}{m^3} = 9.93 \frac{kg}{hr}$$

The molar feed for stream 18 should be the same flows and compositions as stream 17, since only the temperature of the solution is changing.

With the molar flow rate of the feed into the membrane known per module, it is then necessary to determine how much energy is required to heat the bioreactor fluid to the required temperature for optimum membrane operation. This was done using a simple energy balance. A bulk heat capacity for that of water was assumed, once again because the liquid is predominantly water.

$$q_{H-211} = m_{17} * C_p * \Delta T$$

$$q_{H-211} = 91853.5 \frac{kgmol}{hr} * \frac{18.02\ kg}{1\ kgmol} * \frac{1\ hr}{3600\ s} * 4.18 \frac{kJ}{kg*K} * (80 - 42)℃ = 73.0\ MW$$

The heating requirement above was used to determine the necessary steam flow rate through the heat exchanger. This flow rate was found once again using another energy balance. The steam was assumed to be saturated vapor as it entered the heat exchanger and was assumed to be saturated liquid as it left the heat exchanger. The heating fluid would also remain at a pressure of 3500 kPa, which has a saturation temperature of approximately 242 ℃ according to steam tables.[42] Steam at these conditions also has a heat of vaporization of approximately 1752.8 kJ/kg.

$$q_{H-211} = m_{27} * \Delta H_{vap}$$

$$73.0 * 10^3\ kJ = m_{27} * 1752.8 \frac{kJ}{kg}$$

$$m_{27} = 41.66 \frac{kg}{s}$$

The molar flow rate for the steam can also be determined using a couple of simple unit conversions.

$$n_{27} = 41.66 \frac{kg}{s} * \frac{1\ kgmol}{18.02\ kg} * \frac{3600\ s}{1\ hr} = 8374 \frac{kgmol}{hr}$$

Also, the electric heater was assumed to be 90% efficient. This means that the duty on that piece of equipment can also be calculated, using the required heat load on H-211.

$$q_{B-211} * 0.9 = q_{H-211}$$

$$q_{B-211} = \frac{q_{H-211}}{0.9} = \frac{73.0\ MW}{0.9} = 81.5\ MW$$

The molar flow rate through stream 27 is the same as the molar flow rate through streams 28 and 29, as it is just a closed loop. As such, no water will be gained or lost throughout the system.

The duty on P-211 can also be calculated, using a simple mechanical energy balance. The saturated liquid is assumed to not change in fluid velocity or height, meaning all shaft work will come exclusively from a pressure change. The heat exchanger was assumed to have a pressure drop of 10 kPa through it, so the required shaft work can be calculated below.

$$m\left(\frac{\Delta P}{\rho} + \frac{1}{2}v^2 + g\Delta z\right) = w_s$$

$$m\left(\frac{\Delta P}{\rho}\right) = \frac{8374\frac{kgmol}{hr}*\frac{1\ hr}{3600\ s}*\frac{18.02\ kg}{kgmol}*10^4\ Pa}{1000\frac{kg}{m^3}} = 419\ W = w_{s,P-211}$$

Now for the membrane calculations. All of the data used for these calculations concerning ammonia selectivity, ammonia flux, and membrane efficiency are all taken from the paper from CSIRO.[39] A mass balance was done to determine the amount of ammonia that would be transferred across the membrane, as well as the amount of water that would be transferred across the membrane. An efficiency of 95% was assumed, and a selectivity of 5 was also chosen.

$$n_{NH_3,33} = 0.95 * n_{NH_3,18} = 0.95 * \frac{2.26\ kgmol}{hr} = 2.15\frac{kgmol}{hr}$$

$$n_{H_2O,33} = \frac{1}{5} * n_{NH_3,33} = \frac{2.15\frac{kgmol}{hr}}{5} = 0.43\frac{kgmol}{hr}$$

Using a mass balance on the ammonia and the water, the molar flow rates through stream 20 can also be determined. The flow through stream 18 should add to the flows from streams 33 and 20.

$$n_{NH_3,20} = n_{NH_3,18} - n_{NH_3,33} = 2.26\frac{kgmol}{hr} - 2.15\frac{kgmol}{hr} = 0.11\frac{kgmol}{hr}$$

$$n_{H_2O,20} = n_{H_2O,18} - n_{H_2O,33} = 0.999975 * 91853.5\frac{kgmol}{hr} - 0.43\frac{kgmol}{hr} = 91850.8\frac{kgmol}{hr}$$

Then, the molar composition for stream 20 can also be calculated.

$$x_{NH_3,20} = \frac{\left(0.11\frac{kgmol}{hr}\right)}{(91850.8+0.11)\frac{kgmol}{hr}} = 1.19 * 10^{-4}\%\ NH_3$$

$$x_{H_2O,20} = 100 - 0.0025 = 99.9999\%\ H_2O$$

The molar flow rate for stream 21 are the same as for stream 20, because it only undergoes a temperature change.

The molar flow rate for stream 25 and 26 can be calculated similarly to the calculations for streams 27, 28, and 29. Using the required heat transferred and some assumed fluid properties, this flow rate can be calculated.

$$q_{H-211} = m_{25} * C_p * \Delta T$$

$$73.0 * 10^3\frac{kJ}{s} = m_{25} * 4.18\frac{kJ}{kg*K} * (40-30)℃$$

$$m_{25} = 1746\frac{kg}{s}$$

This flowrate can be transformed into a molar flow rate by using the molar mass of water. And this molar flow rate will hold for stream 26 as well.

$$n_{25} = 1746\frac{kg}{s} * \frac{1\ kgmol}{18.02\ kg} * \frac{3600\ s}{1\ hr} = 349000\frac{kgmol}{hr}$$

Streams 20, 21, 31, and 22 will all have the same concentrations. It was assumed that the plant would have to remove 5% of its total volume every week. This was used to determine the molar flow rate of stream 31.

$$n_{31} = 0.05 * n_{total} = 0.05 * \frac{2383488\ m^3*1000\frac{kg}{m^3}*\frac{kgmol}{18.02\ kg}*\frac{1}{60\ modules}}{1\ week*\frac{7\ days}{week}*\frac{24\ hr}{day}} = 656.1\frac{kgmol}{hr}$$

The total molar flow rate for stream 22 is just the difference between the flows of 31 and 21, based on a mass balance.

$$n_{22} = n_{21} - n_{31} = 91850\frac{kgmol}{hr} - 656.1\frac{kgmol}{hr} = 91194\frac{kgmol}{hr}$$

The molar flow rate for stream 30 is meant to balance out what is lost via the cell medium waste stream, so its molar flow rate should equal that of 31.

Stream 23 should have the same concentration and flow rate as stream 21, except for the addition of the cyanobacteria back into the system. Stream 24 should have the same properties as stream 23, since it has only undergone pumping to move the medium to the front of the bioreactor.

The duty on pump P-212 can be calculated using a mechanical energy balance. It was assumed that there would be no pressure change, nor any change in fluid velocity. P-212 only is required to increase the height of the fluid from the mixing tank up to the height of the bioreactor inlet, which is 7 meters above.

$$\dot{m}\left(\frac{\Delta P}{\rho} + \frac{1}{2}v^2 + g\Delta z\right) = \dot{w}_s$$

$$\dot{m}(g\Delta z) = 1655.2\,\frac{m^3}{hr} * 1000\,\frac{kg}{m^3} * 9.8\,\frac{m}{s^2} * 7\,m * \frac{1\,hr}{3600\,s} = 31.5\,kW = \dot{w}_{s,P-212}$$

It was also found from the CSIRO study that a sweep gas flow rate with a volumetric flow rate of 10 times the liquid flow rate was required.[39] So, using this value, a volumetric flow rate for the air sweep gas could also be calculated.

$$\dot{V}_{32} = 10 * \dot{V}_{32} = 10 * 2383488\,\frac{m^3}{day} * \frac{1\,day}{24\,hr} * \frac{1}{60\,modules} = 16552\,\frac{m^3}{hr}$$

This volumetric flow rate can be transformed into a molar flow rate using the molar density of the gas. To find this, the air was assumed to act as an ideal gas, because it is at room temperature and at a low pressure of 17.33 kPa. The ideal gas law could be manipulated to determine a molar density for the air at these conditions.

$$\frac{V}{n} = \frac{RT}{P} = \frac{\left(8.314\frac{J}{mol*K}*\frac{1000\,mol}{kgmol}*293\,K\right)}{17.33*10^3\,Pa} = 140.56\,\frac{m^3}{kgmol}$$

At this point, the molar flow rate can be determined by dividing the volumetric flow rate by the molar density. This is done below. It is worth noting that the sweep gas is 79% nitrogen gas and 21% oxygen gas, as is usual for air.

$$\dot{n}_{32} = \frac{\dot{V}_{32}}{\frac{V}{n}} = \frac{16552\frac{m^3}{hr}}{140.56\frac{m^3}{kgmol}} = 117.8\,\frac{kgmol}{hr}$$

With all the component molar flows known for stream 3.4, the molar composition can also be calculated.

$$x_{NH_3,33} = \frac{\left(2.15\frac{kgmol}{hr}\right)}{(117.8+2.15+0.43)\frac{kgmol}{hr}} = 1.8\%\ NH_3$$

$$x_{H_2O,33} = \frac{\left(0.43\frac{kgmol}{hr}\right)}{(117.8+2.15+0.43)\frac{kgmol}{hr}} = 0.3\%\ H_2O$$

$$x_{N_2,33} = \frac{0.79*\left(117.8\frac{kgmol}{hr}\right)}{(117.8+2.15+0.43)\frac{kgmol}{hr}} = 77.4\%\ N_2$$

$$x_{O_2,33} = \frac{0.21*\left(117.8\frac{kgmol}{hr}\right)}{(117.8+2.15+0.43)\frac{kgmol}{hr}} = 20.5\%\ O_2$$

At this point, all the material and energy streams are fully defined for the membrane section.

Absorber/Desorber

To recover the ammonia from the compressed air permeate, two methods were considered: condensation/separation and absorption. Due to the low concentration of ammonia (1.8 mol %) in the air mixture, Aspen HYSYS simulations with a NRTL-RK fluid model suggested a temperature of -161 ℃ was required to condense the ammonia and remaining water out of the air. The high overall flowrate (7212 kmol/hr) made the overall cooling duty significant, and cryogenic refrigeration cycles had total compression duties of 146 MW. This was an unreasonably high energy requirement, and further complications were present in separating the remaining water and ammonia downstream since ammonia is highly soluble in water. The condensation and separation of vapor and liquid phases in traditional Haber-Bosch processes is possible because the reactor products are already compressed, and a much higher ammonia composition (in the range of 20-40 mol%) allows for condensation at a temperature closer to the pure ammonia normal boiling point of -33 ℃. Due to the complications with the low ammonia composition and remaining water from the membrane, an alternative selective absorption method was evaluated.

The viability of the novel selective absorption method has been experimentally and theoretically confirmed for small-scale ammonia production. The article "Modeling and Optimal Design of Absorbent Enhanced Ammonia Synthesis" by Palys et al provides a method for up to 10,000 kg/hr ammonia production through a 40 wt% $MgCl_2$ and 60 wt% silica gel selective absorbent for ammonia. A major difference in our proposed design is the presence of oxygen and trace amounts of water, whereas experimental studies were based on the traditional Haber-Bosch reaction with hydrogen, nitrogen, and ammonia as the mixture requiring absorption. While silica gel is a desiccator that absorbs water, further research suggested it desorbs water at atmospheric pressure and temperatures of 150 ℃ and above. Thus, maintaining the absorption/desorption conditions above 150 ℃ ensures water does not absorb. While the study did not have oxygen in the system, further research suggested oxygen is unlikely to absorb in $MgCl_2$, but rather reacts with it at temperatures above 500 ℃. Using these constraints, the absorption/desorption conditions were determined through mass transfer principles.

The absorption rate of nitrogen, oxygen, and water can be assumed as zero since the absorbent chosen is selective to ammonia and operates at temperatures that limit water absorption. A relation from Palys' article relates the absorbent's equilibrium pressure to temperature.

$$P_{eq} = \exp\left(-\frac{\Delta H_{abs}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$

Where, P_{eq} is the equilibrium pressure of the absorbent (bar), ΔH_{abs} is the enthalpy of absorption (87,000 J/mol), R is the gas constant (J/K-mol), T is the temperature of absorption (K), and T_{ref} is the reference temperature that the enthalpy of absorption was based on (648.05 K). For absorption, the partial pressure of ammonia must be greater than the equilibrium pressure of the absorbent. For desorption, the ammonia partial pressure must be less than the equilibrium pressure of the absorbent. Relations from Palys' provide a description of absorption and desorption rates.

$$r_{abs} = \frac{k_{abs}\left(P_{NH_3} - P_{eq}(T)\right)^7}{K_{abs} + \left(P_{NH_3} - P_{eq}(T)\right)^6}$$

$$r_{des} = k_{des}\left(P_{eq}(T) - P_{NH_3}\right)$$

Where, the rate constant parameters are defined as follows:

K_{abs} = 5x10^{-24} bar^6

k_{abs} = 0.4668 mol NH_3/(kg$_{abs}$-bar-s)

k_{des} =7.002x10^{-3} mol NH_3/(kg$_{abs}$-bar-s)

The feed to the absorber required compression since the membrane permeate was at a vacuum pressure of 17.33 kPa. Furthermore, desorption is only possible through heating to desorption conditions and then lowering the pressure at one end of the packed bed. The pressure gradient then forces the purified ammonia out of the absorber. Due to the high flowrate of the air and ammonia mixture, compression energy requirements were significant. The feed was compressed to 150 kPa for absorption, which had an energy requirement of 317 kW per module, or 20 MW for the overall plant. While this is still a high energy requirement, it is a significant improvement from the method of condensing ammonia out of the mixture. At 150 kPa, the partial pressure of ammonia was 0.025 bar. To ensure the absorption temperature was above 150 ℃ (to prevent water absorption) and that the equilibrium pressure of the absorbent was less than the partial pressure of ammonia, a range of temperatures were analyzed for the equilibrium pressure equation. At 200 ℃, an equilibrium pressure of 0.00254 bar provided a reasonable absorption rate of 0.0104 mol NH_3/kg$_{abs}$-s. The best method for improving absorption rates was to lower temperature or raise the overall pressure. This created a tradeoff between the possibility of absorbing water into the silica gel, increasing compression requirements for the feed, and obtaining faster absorption cycles. With the constraints of the system, this absorption rate was acceptable given the absorbent capacity of 0.0714 kg NH_3 per kg absorbent.

Since this method of absorption and desorption is not a continuous process, it was decided to implement four absorbers per module, with each operating at a different point of the cycle: absorption, heating, desorption, and then cooling back to absorption conditions. It was thus imperative to have the same absorption and desorption rates to approximate a continuous process. Using the desorption pressure of 1 bar, a desorption rate equivalent to the absorption rate of 0.0104 mol NH_3/kg$_{abs}$-s was found at a temperature of 392 ℃. A conservative temperature ramp time of 6.7 minutes was chosen because the absorption and desorption times were also 6.7 minutes. Ensuring each stage in the cycle was the same time, the 4 absorbers in parallel essentially act as one continuous unit. For both absorption and desorption, it took 6.7 minutes to reach capacity, which provided a total cycle time of 29.7 minutes, and 48 cycles per day.

At 48 cycles per day, 2190 kg/hr of ammonia was absorbed and desorbed. A total of 16,042 kg absorbent was required, based on both the absorbent capacity and a 10% design factor. It was suggested that a length to diameter ratio of at least 2 was used in designing the absorber. For simplicity, a jacketed vessel was chosen to heat and the absorbent for absorption/desorption cycles. However, heating considerations and residence times for the solid packed bed of absorbent led to an L/D of 14, with the length and diameter being 4 m and 0.146 m, respectively, for each absorber in each module. This was further based on an assumed void fraction of 0.4 in the packed beds. The relatively small diameter allowed for efficient and uniform heating of the absorbent during the absorption/desorption cycle. Inductive heating coils were used in the jacketed vessel for this purpose. Finally, it was assumed that although the temperature of absorption was above the desorption temperature of water, some water may have been absorbed in the process. Thus, the ammonia product was estimated to be 99.6 wt% ammonia and 0.4 wt% water.

Design of the heat exchangers in the purification section was accomplished through material and energy balances. The heat exchanger design equation is as follows:

$$A = \frac{Q}{U\Delta T_{lm}}$$

Where, *A* is the required heat exchange area (m^2), *U* is the overall heat transfer coefficient (W/m^2-K), and *Q* is the rate of heat transfer. As a sample calculation, the required heat transfer rate for the heat exchanger after compression of the gas mixture to 1.5 bar (H-312) was determined in HYSYS to be 184 kW. For cooling a gas mixture, a suggested overall heat transfer coefficient of 30 W/m^2-K was used. The log-mean temperature difference was calculated as follows, where the gas was cooled from 377 ℃ to 200 ℃ and the cooling water was fed at 20 ℃ with a 30 ℃ allowable temperature rise. All heat exchangers were operated in a counter-current configuration to maximize the temperature driving force and thus minimize cooling water requirements.

$$\Delta T_{lm} = \frac{\Delta T_2 - \Delta T_1}{\ln\left(\frac{\Delta T_2}{\Delta T_1}\right)} = \frac{(377 - 50\ ℃) - (200 - 20\ ℃)}{\ln\left(\frac{(377 - 50\ ℃)}{200 - 20\ ℃}\right)} = \mathbf{246}\ ℃$$

Where, ΔT_2 is the temperature difference between the hot and cold fluid at one end of the heat exchanger (K or ℃), and ΔT_1 is the temperature difference between the hot and cold fluid at the other end of the heat exchanger (K or ℃). The hot fluid is the ammonia/air mixture, and the cold fluid is the refrigerant. Using this value, the required heat transfer area was calculated:

$$A = \frac{Q}{U\Delta T_{lm}} = \frac{184\ kW}{\left(30\frac{W}{m^2K}\right)(246\ K)}\left(1000\frac{W}{kW}\right) = \mathbf{24.8\ m^2}$$

After getting the required heat exchanger area for one module, the diameters and number of tubes for a shell & tube heat exchanger were determined. A shell and tube heat exchanger was used due to its wide application in industry, ease of cleaning and maintenance, and ability to fit a large amount of heat transfer area in a compact space. Towler and Sinnott's *Chemical Engineering Design* provided some Tubular Exchanger Manufacturers Association (TEMA) standard diameters and lengths that were used in heat exchanger sizing. The tube inner diameter was chosen as 16 mm, the tube wall thickness was 1.7 mm, and the length was chosen as 1.83 m (6 ft). The number of tubes was then determined using the following equation.

$$N_t = \frac{A}{\pi d_i L}$$

Where. N_t is the number of tubes, d_i is the inner diameter of the tube (m), *A* is the tube heat exchanger area (m^2), and *L* is the tube length (m). The area for each tube and the number of tubes for H-312 were as follows, where a 10% design factor was added for the number of tubes.

$$A = \pi(0.0016\ m)(1.83\ m) = 0.092\ m^2$$

$$N_t = \frac{0.092\ m^2}{\pi(0.0016\ m)(1.83\ m)}(1.1) = 300$$

For a compact tube bundle, a triangular pitch was selected to provide a high heat transfer rate at the cost of a higher pressure loss compared to a square pitch. The following image provides a cross-section of 1 triangular bundle of tubes.

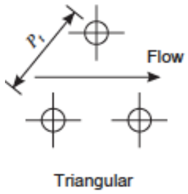


Figure 61. Triangular tube arrangement, where p_t denotes the tube pitch spacing (m). This image was taken from Figure 19.10 of Towler and Sinnott's *Chemical Engineering Design*.

The standard pitch spacing was 1.25 times the tube outer diameter. Given the number of tubes and the pitch spacing, the tube bundle diameter can be determined with the following equation.

$$D_b = d_o \left(\frac{N_t}{K_1}\right)^{1/n_1}$$

Where, D_b is the bundle diameter (m), d_o is the tube outer diameter (m), and K_1 and n_1 are constants dependent on the number of tube passes and pitch. The standard Type E heat exchanger was chosen for ease of maintenance, with only 1 tube pass. Table 19.4 in Towler and Sinnott's *Chemical Engineering Design* provides constants of 0.319 and 2.142 for K_1 and n_1, respectively. These values yielded a bundle diameter of:

$$D_b = (0.00177\ m)\left(\frac{300}{0.319}\right)^{1/2.142} = \mathbf{0.43\ m}$$

Finally, a graph of the shell-bundle clearance in Figure 19.12 of Towler and Sinnott's *Chemical Engineering Design* provides recommended shell diameters at varying bundle diameters for a Fixed and U-tube heat exchanger. The TEMA standard for shell thickness ranged from 10-25 mm. As a conservative estimate, the shell diameter was 1.4 cm larger than the bundle diameter, and the shell thickness was 2.5 cm (accounting for 2 mm of corrosion allowance). To improve heat transfer, 7 mm diameter baffles were installed based on recommended spacing of half the shell diameter.

$$N_b = \frac{L}{0.5 D_{shell,outer}} = \frac{1.83m}{0.5(0.47\ m)} = 7$$

These same calculations were used for all heat exchangers in the purification section, and a quick summary is shown in the following table. For condensing ammonia, literature suggested an overall heat transfer coefficient of 500 W/m^2-K would be sufficient. Lastly, the required cooling water flowrate (n, per module) was determined in Aspen HYSYS.

Equipment #	**$\dot{n}$ (kmol/hr)**	**U (W/m^2-K)**	**ΔT_{lm} (°C)**	**A (m^2)**	**N_t**	**D_b (m)**	***Shell ID* (m)**	**N_b**
H-312	290	30	246	24.8	300	0.43	0.45	7
H-313	12.7	30	128	2.08	35	0.14	0.15	20
H-315	90.4	500	92	0.42	6	0.07	0.08	34

The material balance and design for the anhydrous ammonia storage tanks is discussed in the next section.

Anhydrous Ammonia Storage Pressure Vessel

The purified ammonia product from selective absorption is processed for storage through a pre-compression cooler, a compressor to 200 psia, and another heat exchanger to condense the product as a liquid. The ASME Boiler and Pressure Vessel Code suggested anhydrous ammonia is typically stored at 200 psia, and that storage vessels are rated for 250 psig with a 15% vapor space available if expansion. At 200 psia, anhydrous ammonia is a liquid at 38.12 °C. It was chosen to subcool the ammonia to 30 °C, which provided enough temperature driving force for the cooling water rise from 20 °C to 30 °C in a counter-current configuration. In Minnesota, average temperature range from 0-28 °C. Atmospheric temperatures only serve to further sub-cool the liquid, and thus it was deemed unnecessary to cool the condensed product further. This heat exchanger design (H-315) was discussed in the previous section. The compressor duty was 7.1 kW for each module, or a total of 427 kW for the whole plant. Using the assumption that kinetic and potential energy could be neglected, and that the compressor was adiabatic and reversible, the temperature after compression was determined in Aspen HYSYS as 370 °C. Thus, another heat exchanger was used to cool and condense the product.

After liquefying the anhydrous ammonia product, it was sent to storage pressure vessels. Assuming daily shipments of the ammonia product, 60 storage vessels were designed, with a total required volume calculated as follows.

$$V_{storage} = \frac{m}{0.85\rho}$$

Where, m is the total mass of ammonia produced per day (50,000 kg/day), and ρ is the density of the liquefied ammonia at 200 psia and 38 °C (598.7 kg/m^3). A factor of 85% was used to allow for head space of the vessel in case of expansion.

$$V_{storage} = \frac{50000\ kg}{(0.85)\left(598.7\frac{kg}{m^3}\right)} = 98.3\ m^3$$

Using an L/D ratio of 5, the diameter and length for each vessel were 0.75 m and 3.74 m, respectively. Assuming a cylindrical body and hemispherical ends of the storage vessel, the surface area was determined to be 10 m^2. Material compatibility research suggested stainless steel received an “A” rating for ammonia. Thus, SS 304 was chosen since it was slightly cheaper than SS 316 and had the same compatibility. The design pressure was 250 psig, and the maximum allowable stress, *S*, for SS 304 was 20 ksi (ASME BPV Code Sec. VIII D.1). An assumed efficiency of 85% was chosen (spot radiographic examination, double-welded butt joint). Both the hoop stress and longitudinal stress thicknesses were examined.

$$\sigma_{hoop} = \frac{P_{design}D}{2SE - (1.2P_{design})} = \frac{(0.25\ ksi)(0.75\ m)}{2(20\ ksi)(0.85) - (1.2)(0.25\ ksi)} = 0.0055\ m$$

$$\sigma_{longitudinal} = \frac{P_{design}D}{4SE + (0.8P_{design})} = \frac{(0.25\ ksi)(0.75\ m)}{4(20\ ksi)(0.85) + (0.8)(0.25\ ksi)} = 0.0027\ m$$

The more conservative thickness was chosen (hoop stress), and an extra 2 mm were added on for corrosion allowance providing a total wall thickness of 7.5 mm. Towler and Sinnott’s *Chemical Engineering Design* Section 14.4.8 has a suggested wall thickness of 5 mm for vessels with a diameter of 1 m, which provides confidence that the chosen wall thickness of 7.5 mm is within industry standards. Using a SS 304 density of 7900 kg/m^3, the shell mass for each storage vessel was found as 123 kg. Further discussion on the design and process safety of the pressure vessels is provided in Section XV (Process Safety Considerations). Simulation results from Aspen HYSYS, which informed much of the design, are provided in the Appendix.

VII. Utility Requirements

Energy Sources

Oil & natural gas or coal are common energy sources for ammonia production plants, which presents a problem due to the significant energy requirements and harmful emissions that can be created through these traditional sources. Wind energy was selected to meet the energy requirements of the plant because of the significant wind present in southwestern Minnesota and its recent technological advances in renewable energy applications. The traditional horizontal-axis wind turbine design was selected due to the large-scale energy requirements expected for the plant. Other wind turbines, such as a vertical-axis wind turbine, is typically used on a smaller scale.

Although wind is an extremely clean source of energy during the lifespan of a wind turbine, it has a few disadvantages in the form of post-life waste production and manufacturing methods. Furthermore, during its lifetime, wind turbines can harm birds and take up a significant area of land. Control systems and radar have allowed wind turbines to shut off when a flock of birds approaches, which largely solves that common criticism, and is recommended to be implemented into this design. The manufacture and disposal of some turbine parts can be environmentally harmful because it requires the mining of some rare earth metals. Another significant drawback is the large capital cost incurred by wind turbines. Although maintenance and operational costs tend to be minimal, the payback period for wind turbines can be extensive as opposed to using traditional fossil fuel energy sources.

The power generated by a wind turbine is proportional to the cube of the wind velocity. This is beneficial in Minnesota, as high wind speeds significantly improve wind energy production rates. Similarly, a large cross-sectional area of the blades is often more effective at capturing wind energy. Fluid dynamics have explained a drop in wind speed when crossing turbine blades. This phenomenon has led to an efficiency coefficient for turbines. The ideal power efficiency coefficient is 59% for wind turbines. The following derivation expands on the principles of wind energy production, starting from the kinetic energy of wind.

$$KE = \frac{1}{2}mv^2$$

$$m = \rho_{air}V$$

$$V = A(v)(time)$$

$$J = \frac{KE}{t} = \frac{1}{2t}\rho_{air}Av^3t$$

$$J = \frac{1}{2}\rho_{air}Av^3C$$

Where, J is the power output (kW), ρ_{air} is the average air density (kg/m^3), A is the cross-sectional area covered by the wind turbine blades (m^2), v is the velocity of the wind (m/s), and C is a power efficiency coefficient. These equations emphasize the dependence of energy production on the cross-sectional area of the blades and the cube of the wind speed.

Some alternative renewable energy sources were examined due to the capital-intensive nature of wind energy. Preliminary research suggested solar energy would not be effective on a large-scale in Minnesota because it is typically sunny or partly sunny for only 52-58% of the year, and solar panels produce only 10-25% of their typical power on cloudy days as opposed to sunny days. This suggested a larger volume of solar panels would be required to make up for a lack of productivity, and thus it would have a similar capital-intensive problem as wind energy. Hydrolectric power makes up a small portion of Minnesota’s overall energy sources and requires significant capital investment for a large-scale, and thus was ruled out as an energy source for the plant. Since a primary objective of this plant is to minimize greenhouse gas emissions and natural gas consumption, wind energy is believed to be necessary for fully fossil-fuel independent production of anhydrous ammonia. As a capital-intensive energy source, wind energy may prove to be unprofitable, however it provides an avenue for future ammonia plant production as technology improves.

Energy Storage

One concern of wind energy is its inconsistent energy delivery, however energy storage technologies in recent years have significantly improved. Common energy storage techniques include compressed air storage, batteries, or pumped-storage hydroelectricity. While research suggested compressed air was the cheapest energy storage method, its disadvantages eliminated it from consideration. Compressed air requires using some of the wind energy to compress the air, and the heat energy associated with compression would also have to be conserved. Extracting the energy from compressed air was also deemed inefficient, as it required further heating to expand air. Pumped-storage hydroelectricity was also not feasible on a large-scale, as hydroelectric power makes up only a small portion of energy sources Minnesota. Consequently, battery storage was settled on. Using a 2019 U.S. Department of Energy *Energy Storage Technology and Cost Characterization Report*, the costs and efficiencies of differing battery types were examined, including sodium-sulfur (NaS), Lithium-ion, Lead-acid, sodium metal halide, zinc-hybrid cathode, and redox flow battery. The following table summarizes key performance indicators such as energy capacity ($/kWh), construction & commissioning ($/kWh), total cost ($/kW), fixed operating costs ($/kW-yr), efficiency, and life-time. The initial capital costs and future investment costs for replacement were then converted to an amortized cost for each battery. For example, the initial cost of a 1 MW sodium sulfur (NaS) battery is annualized over its lifetime, *n*, through the capital recovery factor equation (an interest rate, *i*, of 8% was assumed for all cases).

$$A = \frac{Pi(1+i)^n}{(1+i)^n - 1} = \frac{\left(\frac{\$3626}{kW}\right)(1000\ kW)(0.08)(1.08)^{13.5}}{1.08^{13.5} - 1} = \$\mathbf{448,900}\ per\ 1\ MW\ battery$$

This calculation was conducted for a 1 MW battery for each battery type, and is summarized in the following table.

	NaS	**Li-ion**	**Lead-Acid**	**Sodium Metal Halide**	**Zinc-Hybrid Cathode**	**Redox Flow Battery**
Energy Capacity ($/kWh)	661	271	260	700	265	555
Construction & Commissioning ($/kWh)	133	101	176	115	173	190
Total Cost ($/kW)	3626	1876	2194	3710	2202	3430
Fixed Operating Costs ($/kW-yr)	10	10	10	10	10	10
Efficiency	0.75	0.86	0.72	0.83	0.72	0.675
Life-time (years)	13.5	10	2.6	12.5	10	15
Total Initial CAPEX ($)	$3.63M	$1.88M	$2.19M	$3.71M	$2.2M	$3.43M
Annualized Cost ($/yr)	$448,900	$279,600	$967,900	$480,400	$328,200	$400,800

As recent battery data and economic calculations suggest, lithium-ion batteries are currently the most economical form of large-scale battery energy storage. The recurring future investment costs of replacing batteries during the plant's lifetime were not accounted for here, as lithium-ion batteris had both the lowest annualized cost based on 1 lifetime, and one of the longest lifetimes. This led to the data-driven decision to use lithium-ion batteries as the energy storage method for the plant.

Another concern with energy storage is ensuring there is a constant delivery of electricity to the plant to ensure continuous daily operation. A 2009 *IEEE* article on “Control Strategies for Battery Energy Storage for Wind Farm Dispatching” proposes methods to smooth out energy storage and delivery by using hourly wind farm data and predictions. It is recommended that during plant start-up, wind energy delivery rates be consistently measured and compared to predictions. This would allow for development of a reasonably accurate dynamic model that can optimize energy delivery and storage. The current storage requirements were conservatively estimated based on the average capacity factor for wind energy in Minnesota; however, this data could allow for a reduction in the storage requirements as the plant’s lifetime proceeds, or for an opportunity to sell electricity for credit.

One advantage of this plant design is that the cyanobacteria consume carbon dioxide as nutrients. Thus, they have the capacity to decrease emissions. A counterpoint to this is the extreme energy requirements for pumping water through the bioreactors. If the energy source were entirely based on wind, millions of 1.5 or 3 MW wind turbines would be required. This is infeasible, and thus a carbon-neutral approach was taken to meet the energy requirements of the plant. Natural gas was used under the constraint that CO_2 emissions were equivalent to the CO_2 removed from the environment via cyanobacteria consumption.

Utility Requirements

Finally, the utility requirements of the plant can be summarized. Key utilities and raw materials include the culture medium, cooling water, pumping and compression, and electric energy for the steam heater.

The culture medium, which is primarily deionized water, has a required weekly 5% refresh of $1.19\text{x}10^8$ L of culture medium.

For the purification section, Aspen HYSYS helped determine overall cooling water requirements. In total, 23,550 kmol/hr of cooling water is required. Assuming a 100% production time, this is the following amount of water:

$$V_{cw} = \frac{\left(23550\,\frac{kmol}{hr}\right)\left(18.03\,\frac{kg}{kmol}\right)\left(\frac{8760\ hr}{yr}\right)}{1000\ kg/m^3} = 3{,}720{,}000\ m^3/yr$$

The total energy requirements for compression were also determined in HYSYS, using a 75% efficiency, and summed up to 21 MW. Finally, the energy requirements to heat the absorbent to 392 ℃ from 200 ℃, using a jacketed vessel, were determined using Fourier’s law of heat conduction.

$$q = -k\frac{dT}{dr}(\pi D L)$$

Where, q is the heat transfer rate (W), k is the thermal conductivity of the absorbent (W/m-℃), dT/dr is the instantaneous temperature change in the radial direction (℃/m), D is the diameter of the absorber, and L is the length of the absorber. It was assumed that heat transfer was unidirectional and uniform, although in reality the heat transfer is likely to be nonuniform. The thermal conductivity of the absorbent was averaged over the temperature range with properties from Welty's 6th edition of *Fundamentals of Momentum, Heat, and Mass Transfer*.

$$q = -\left(1.5\frac{W}{m\,K}\right)\frac{(392-200\ ℃)}{0.073\ m}(\pi(0.146\ m)(4\ m) = 7.2\ kW\ per\ module$$

Over 60 modules, this is a total energy requirement of 430 kW. All utility and raw material requirements are summarized in the following table.

Utility or Raw Material Description	Energy Requirement or Yearly Resource Requirement
Culture medium	$2,785,700,000/yr
Photobioreactor pumping	5045294 MW, $136,843,600/yr natural gas
Steam Heater	81 MW
Cooling Water	3,720,000 m^3/yr
Compression	21 MW
Absorber	430 kW
Total Energy Requirements	5045398 MW

VIII. Equipment List & Unit Descriptions

Equipment No.	Unit Description	Material of Construction	No. Units Per Module	Total No. Units
P-110	Pump for moving cell culture and medium through bioreactor. Repeated every 10 pipes through bioreactor.	Not Specified	28579	1714740
C-111	Centrifuge to remove cyanobacteria intermittently through bioreactor, to prevent cyanobacteria concentration from getting too high. Repeated 18 times throughout photobioreactor.	Likely steel, not specified	18	1080
M-112	Membrane to preliminarily remove ammonia from system throughout photobioreactor, to ensure that the concentration of ammonia does not begin to inhibit cyanobacteria production rate.	Polymeric Membrane	18	1080
M-210	Membrane system to remove ammonia generated by cyanobacteria from bioreactor liquid medium.	Polymeric Membrane	1	60

C-211	Centrifuge to remove cyanobacteria from liquid bioreactor feed into membrane system. Gathered cyanobacteria is waste.	Likely steel, type not specified	1	60
C-212	Centrifuge to remove cyanobacteria from liquid bioreactor feed into membrane system. Gathered cyanobacteria is reintroduced later in the system to keep culture constant.	Likely steel, type not specified.	1	60
HX-211	Heat exchanger to increase temperature of membrane feed to 80°C, for more efficient removal of ammonia in membrane.	316 Stainless Steel, Shell and Tube HX	1	60
HX-212	Heat exchanger to lower the temperature of the cell medium after it has passed through the membrane, to make it an environment hospitable for reintroduction of cyanobacteria.	Carbon Steel, flat plate HX	1	60
B-211	Boiler used to vaporize steam, used as heat transfer fluid through HX-211.	SS-304	1	60
T-210	Mixed tank to reintroduce cyanobacteria to liquid medium. Also serves as a location to introduce new feed into the system, to ensure cyanobacteria are not starved of nutrients.	316 Stainless Steel	1	60
X-311	Compressor for membrane permeate from 17.3 kPa to 150 kPa for absorption and desorption.	SS-304	1	60
H-312	Heat exchanger to cool the compressed air/ammonia and remaining water mixture to absorption conditions of 200 °C.	SS-304	1	60
A-310/320/ 330/340	Absorber/desorber to selectively remove ammonia from the air mixture. Desorption results a higher temperature and lowering the pressure to allow the ammonia to evacuate the chamber. The absorbent is 40 wt% $MgCl_2$ and 60 wt% silica gel.	Carbon-steel	4	240

T-316	Vacuum pump to recycle air and water from absorber back to membrane permeate at 17.3 kPa.	SS-304	1	60
H-313	Heat exchanger to pre-cool the purified ammonia product after the absorber/desorber and prior to being adiabatically compressed.	SS-304	1	60
X-314	Compressor for purified ammonia product storage at 200 psia.	SS-304	1	60
H-315	Heat exchanger to condense ammonia for liquid storage at 200 psia.	SS-304	1	60
T-411	Anhydrous ammonia storage tank.	SS-304	1	60
W-410	Wind turbines.	Fiberglass, Steel	N/A	31,717
W-412	Lithium-ion battery packs for energy storage.	Lithium ion and electrolyte, steel.	N/A	63,434

IX. Equipment Specification Sheets

The equipment specification sheets provide a brief summary of relevant dimensions, operating conditions, and performance characteristics for each major and minor piece of equipment in the plant. The upper left corner of each specification sheet provides the equipment designator as shown in the Process Flow Diagram (PFD). A description of each piece of equipment was provided in the previous section of this report. Although valves are an important part of safe and successful operation of the plant, they were not discussed here. Instead, a discussion on valves used in the plant was provided in Section VII.

C-111	**CENTRIFUGE SPECIFICATION SHEET**	**Page 1 of 1**

Number of Units Per Module: 18
Number of Modules: 60
Total Units: 288
Plant Section: 100-Photobioreactor

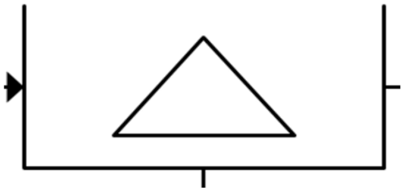
Design Pressure: 101 bar
Operating Pressure: 101 bar

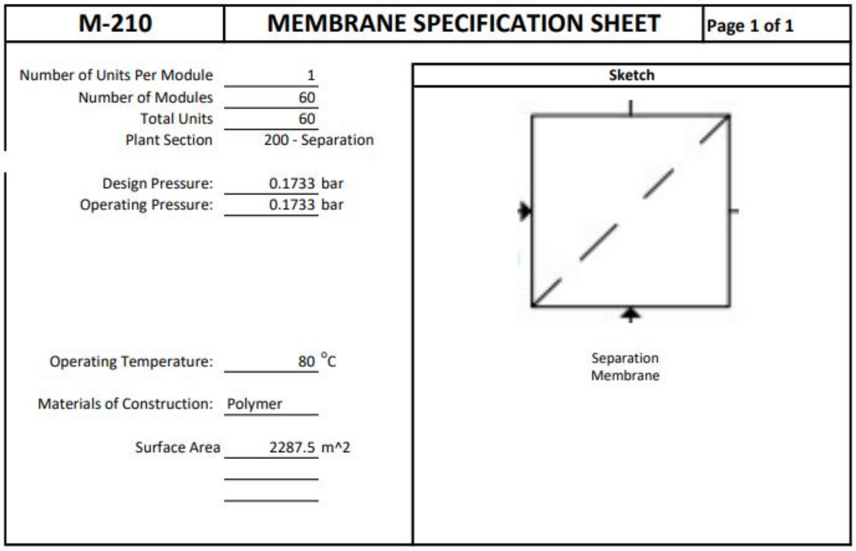
Operating Temperature: 42 °C

Materials of Construction: 316 Stainless

Inlet Flow Rate: 236000 L/hr
Cyanobacteria Removal: 1.66 kg/hr

Sketch





M-210	MEMBRANE SPECIFICATION SHEET	Page 1 of 1

Number of Units Per Module: 1
Number of Modules: 60
Total Units: 60
Plant Section: 200 - Separation

Design Pressure: 0.1733 bar
Operating Pressure: 0.1733 bar

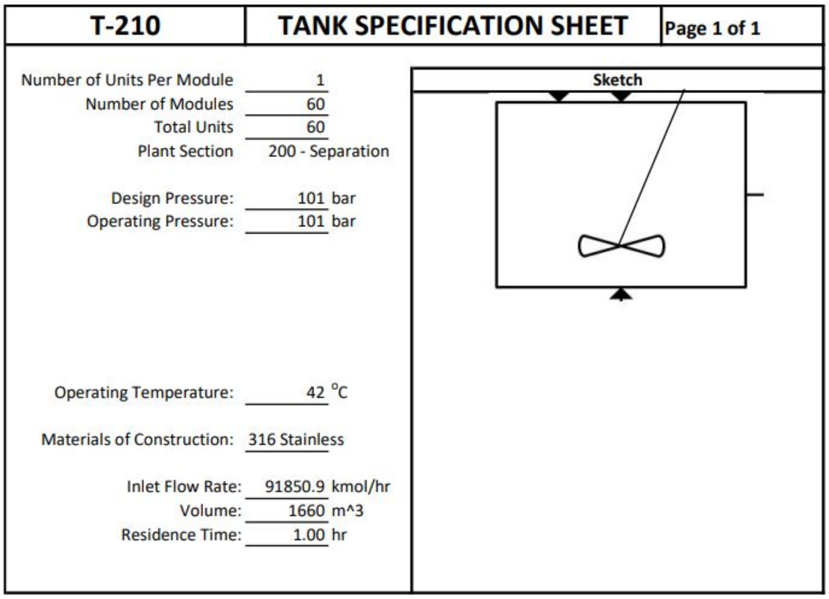
Operating Temperature: 80 °C

Materials of Construction: Polymer

Surface Area: 2287.5 m^2

Sketch

Separation Membrane



T-210 | **TANK SPECIFICATION SHEET** | **Page 1 of 1**

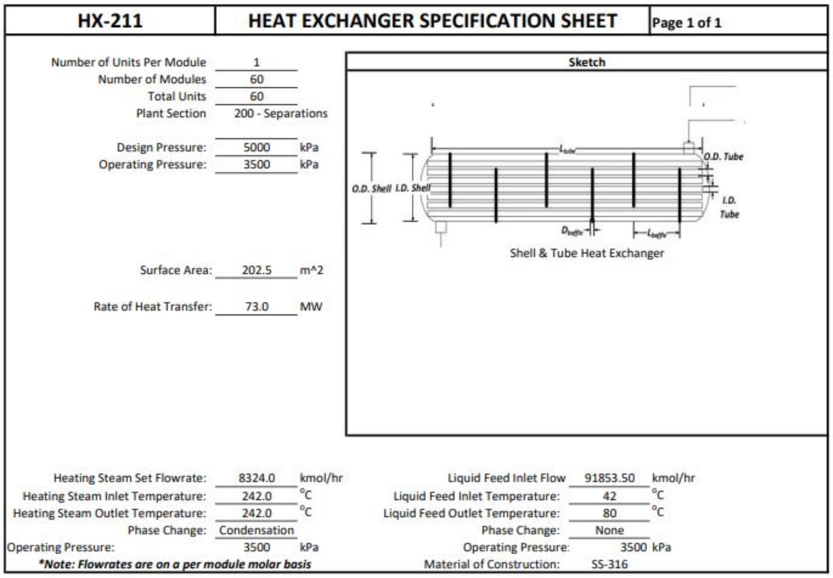
Number of Units Per Module 1
Number of Modules 60
Total Units 60
Plant Section 200 - Separation

Design Pressure: 101 bar
Operating Pressure: 101 bar

Operating Temperature: 42 °C

Materials of Construction: 316 Stainless

Inlet Flow Rate: 91850.9 kmol/hr
Volume: 1660 m^3
Residence Time: 1.00 hr



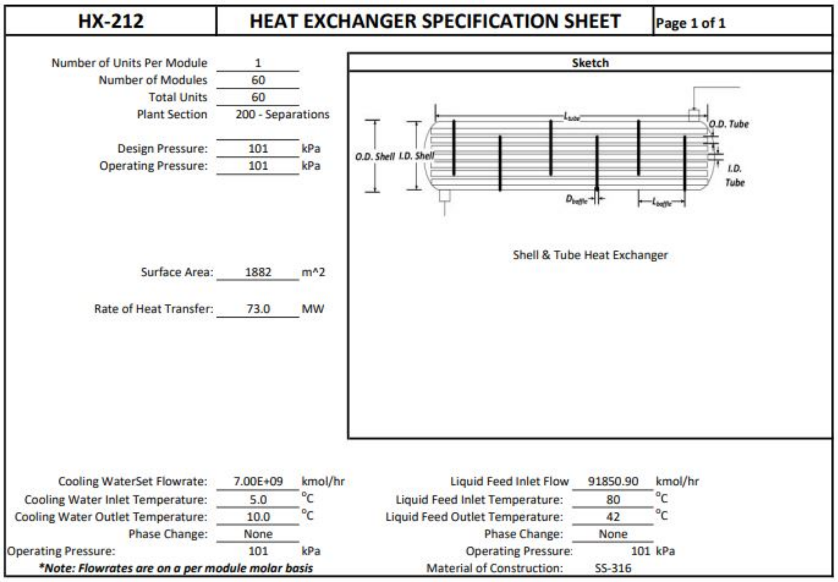
HX-211	HEAT EXCHANGER SPECIFICATION SHEET	Page 1 of 1

Number of Units Per Module	1	
Number of Modules	60	
Total Units	60	
Plant Section	200 - Separations	
Design Pressure:	5000	kPa
Operating Pressure:	3500	kPa
Surface Area:	202.5	m^2
Rate of Heat Transfer:	73.0	MW

Sketch

Shell & Tube Heat Exchanger

Heating Steam Set Flowrate:	8324.0	kmol/hr	Liquid Feed Inlet Flow	91853.50	kmol/hr
Heating Steam Inlet Temperature:	242.0	°C	Liquid Feed Inlet Temperature:	42	°C
Heating Steam Outlet Temperature:	242.0	°C	Liquid Feed Outlet Temperature:	80	°C
Phase Change:	Condensation		Phase Change:	None	
Operating Pressure:	3500	kPa	Operating Pressure:	3500	kPa
***Note: Flowrates are on a per module molar basis**			Material of Construction:	SS-316	



HX-212	**HEAT EXCHANGER SPECIFICATION SHEET**	**Page 1 of 1**

Number of Units Per Module: 1
Number of Modules: 60
Total Units: 60
Plant Section: 200 - Separations

Design Pressure: 101 kPa
Operating Pressure: 101 kPa

Surface Area: 1882 m^2

Rate of Heat Transfer: 73.0 MW

Sketch

Shell & Tube Heat Exchanger

Cooling WaterSet Flowrate:	7.00E+09	kmol/hr	Liquid Feed Inlet Flow	91850.90	kmol/hr
Cooling Water Inlet Temperature:	5.0	°C	Liquid Feed Inlet Temperature:	80	°C
Cooling Water Outlet Temperature:	10.0	°C	Liquid Feed Outlet Temperature:	42	°C
Phase Change:	None		Phase Change:	None	
Operating Pressure:	101	kPa	Operating Pressure:	101	kPa
***Note: Flowrates are on a per module molar basis**			Material of Construction:	SS-316	

B-211	**BOILER SPECIFICATION SHEET**	**Page 1 of 1**

Number of Units Per Module 1
Number of Modules 60
Total Units 60
Plant Section 200 - Separation

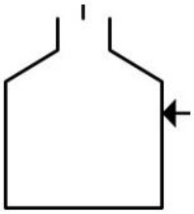
Design Pressure: 10 to 70 bar
Operating Pressure: 35 bar

Operating Temperature: 242 °C

Materials of Construction: 316 Stainless

Efficiency: 90 %
Power Draw 81.1 MW
Steam Flow 150000.00 kg/hr

Sketch



C-211 | **CENTRIFUGE SPECIFICATION SHEET** | **Page 1 of 1**

Number of Units Per Module 1
Number of Modules 60
Total Units 60
Plant Section 200 - Separation

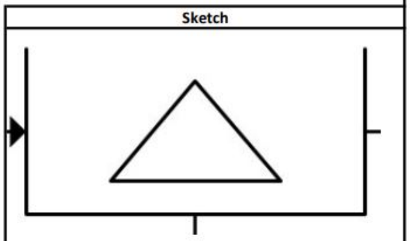
Design Pressure: 101 bar
Operating Pressure: 101 bar

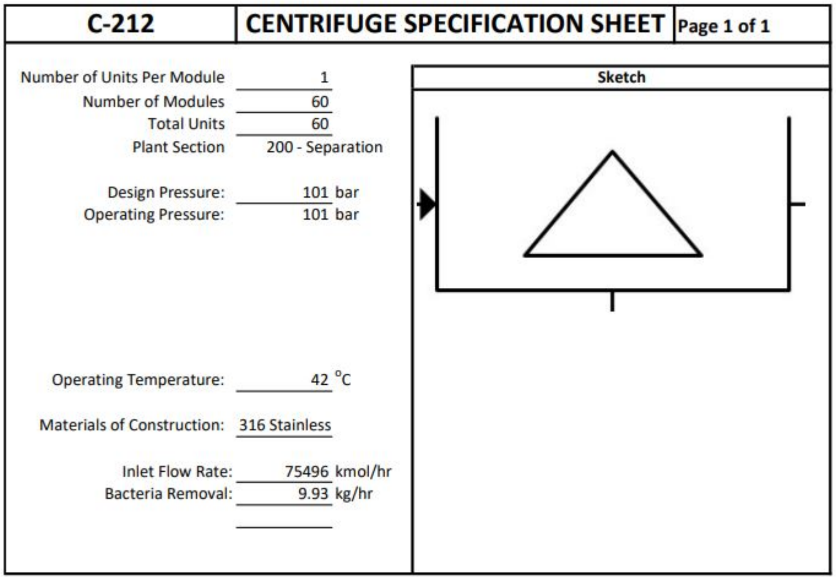
Operating Temperature: 42 °C

Materials of Construction: 316 Stainless

Inlet Flow Rate: 16357.5 kmol/hr
Bacteria Removal: 2.15 kg/hr

Sketch





C-212 | **CENTRIFUGE SPECIFICATION SHEET** | **Page 1 of 1**

Number of Units Per Module: 1
Number of Modules: 60
Total Units: 60
Plant Section: 200 - Separation

Design Pressure: 101 bar
Operating Pressure: 101 bar

Operating Temperature: 42 ^{o}C

Materials of Construction: 316 Stainless

Inlet Flow Rate: 75496 kmol/hr
Bacteria Removal: 9.93 kg/hr

X-311	**COMPRESSOR SPECIFICATION SHEET**	**Page 1 of 1**

Number of Units Per Module 1
Number of Modules 60
Total Units 60
Plant Section 300 - Purification

Design Pressure: 1.65 bar
Inlet Pressure: 0.17 bar
Outlet Pressure: 1.50 bar
Weld Examination: Spot Radiographic, Double-welded butt joint
Joint Efficiency: 85 %
Corrosion Allowance: 2.0 mm

Inlet Operating Temperature: 40.2 °C
Outlet Operating Temperature: 377 °C

Materials of Construction: SS-304

Efficiency: 75 %
Energy Requirements: 343 kW

Gas Mixture Flowrate: 120 kmol/hr
NH_3 Mole %: 1.71 %
O_2 Mole %: 20.6 %
N_2 Mole %: 77.4 %
H_2O Mole %: 0.34 %

***Note: Flowrates & energy requirements are on a per module molar basis**

Sketch

Adiabatic Compressor

H-312	HEAT EXCHANGER SPECIFICATION SHEET	Page 1 of 1

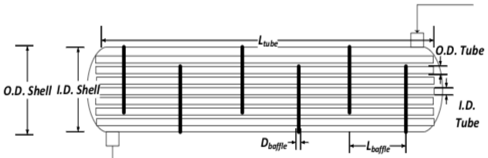
Number of Units Per Module 1
Number of Modules 60
Total Units 60
Plant Section 300 - Purfication

Design Pressure: 1.65 bar
Operating Pressure: 1.50 bar
Weld Examination: Fully Radiographed, Double-welded butt joint
Joint Efficiency: 85 %
Corrosion Allowance: 2.0 mm

Number of Tubes: 300
Tube I.D.: 16.0 mm
Tube O.D.: 17.7 mm
Tube Bundle Diameter: 0.43 m
Shell I.D.: 0.45 m
Shell O.D.: 0.47 m
Length: 1.83 m

Baffle Diameter: 7 mm
Number of Baffles: 7
Baffle Spacing: 0.26 m

Sketch



Shell & Tube Heat Exchanger

Shell			**Tube**		
Cooling Water Set Flowrate:	290	kmol/hr	Gas Mixture Flowrate:	120	kmol/hr
Cooling Water Inlet Temperature:	20	°C	Gas Mixture Inlet Temperature:	377	°C
Cooling Water Outlet Temperature:	50	°C	Gas Mixture Outlet Temperature:	200	°C
Phase Change:	None		Phase Change:	None	
Overall Heat Transfer Coefficient:	30	W/m^2-K	Heat Transfer Area:	24.8	m^2
***Note: Flowrates are on a per module molar basis**			Material of Construction:	SS-304	

A-310/320/330/340	ABSORBER SPECIFICATION SHEET	Page 1 of 1

Number of Units Per Module 4
Number of Modules 60
Total Units 240
Plant Section 300 - Purification

Design Pressure: 1.65 bar

Operating Pressure:

Absorption 1.50 bar
Desorption 1.00 bar

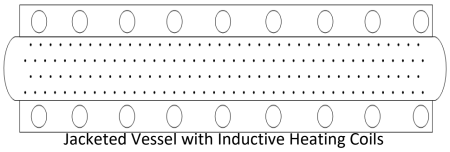
Weld Examination: Spot Radiographic, Double-welded butt joint
Joint Efficiency: 85 %
Corrosion Allowance: 2.00 mm
Wall Thickness: 3.5 mm
Jacket Thickness: m

Operating Temperature:

Absorption 200 °C
Desorption 392 °C

Materials of Construction: Carbon Steel

Sketch



Jacketed Vessel with Inductive Heating Coils

Shell Diameter: 0.146 m
Shell Mass: 668 kg
Shell Length: 4.00 m

Absorbent: 40 wt% $MgCl_2$, 60 wt% silica gel
Absorbent Mass: 66.875 kg
Absorbent Density: 2507 kg/m^3

Absorbent Capacity: 0.0714 kg NH_3/kg_{abs}
Absorption Time: 6.75 min
Desorption Time: 6.75 min

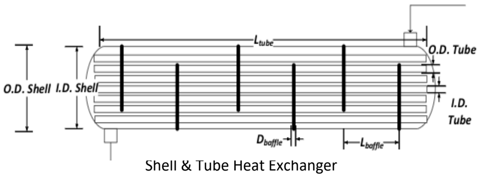
Heating Time: 6.75 min
Cooling Time: 6.75 min
Time per Cycle: 29.7 min

Note: Absorbent mass is on a per unit basis

H-313	**HEAT EXCHANGER SPECIFICATION SHEET**	**Page 1 of 1**

Number of Units Per Module	1	
Number of Modules	60	
Total Units	60	
Plant Section	300 - Purfication	
Design Pressure:	1.1	bar
Operating Pressure:	1.0	bar
Weld Examination:	Fully Radiographed, Double-welded butt joint	
Joint Efficiency:	85	%
Corrosion Allowance:	2.0	mm
Number of Tubes:	26	
Tube I.D.:	16.0	mm
Tube O.D.:	17.7	mm
Tube Bundle Diameter:	0.14	m
Shell I.D.:	0.15	m
Shell O.D.:	0.18	m
Length:	1.83	m
Baffle Diameter:	7	mm
Number of Baffles:	20	
Baffle Spacing:	0.09	m

Sketch



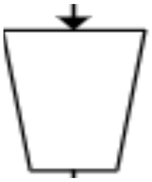
Shell & Tube Heat Exchanger

Shell			**Tube**		
Cooling Water Set Flowrate:	13	kmol/hr	Gas Mixture Flowrate:	2.04	kmol/hr
Cooling Water Inlet Temperature:	20	°C	Gas Mixture Inlet Temperature:	392	°C
Cooling Water Outlet Temperature:	50	°C	Gas Mixture Outlet Temperature:	50	°C
Phase Change:	None		Phase Change:	None	
Overall Heat Transfer Coefficient:	30	W/m^2-K	Heat Transfer Area:	2.1	m^2
***Note: Flowrates are on a per module molar basis**			Material of Construction:	SS-304	

X-314	**COMPRESSOR SPECIFICATION SHEET**	**Page 1 of 1**

Number of Units Per Module	1	
Number of Modules	60	
Total Units	60	
Plant Section	300 - Purification	
Design Pressure:	250	psig
Inlet Pressure:	14.5	psia
Outlet Pressure:	200	psia
Weld Examination:	Spot Radiographic, Double-welded butt joint	
Joint Efficiency:	85	%
Corrosion Allowance:	2.0	mm
Inlet Operating Temperature:	50.0	°C
Outlet Operating Temperature:	361	°C
Materials of Construction:	SS-304	
Efficiency:	75	%
Energy Requirements:	7.1	kW
Gas Mixture Flowrate:	122.3	kmol/hr
NH_3 wt %:	99.6	%
H_2O wt %:	0.04	%

Sketch



Adiabatic Compressor

Note: Flowrates & energy requirements are on a per module molar basis

H-315	HEAT EXCHANGER SPECIFICATION SHEET	Page 1 of 1

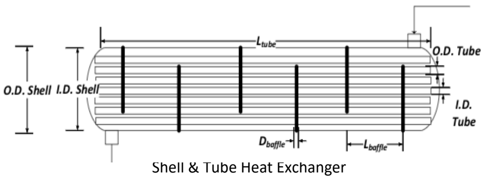
Number of Units Per Module 1
Number of Modules 60
Total Units 60
Plant Section 300 - Purfication

Design Pressure: 220 psia
Operating Pressure: 200 psia
Weld Examination: Fully Radiographed, Double-welded butt joint
Joint Efficiency: 85 %
Corrosion Allowance: 2.0 mm

Number of Tubes: 6
Tube I.D.: 16.0 mm
Tube O.D.: 17.7 mm
Tube Bundle Diameter: 0.07 m
Shell I.D.: 0.08 m
Shell O.D.: 0.11 m
Length: 1.83 m

Baffle Diameter: 7 mm
Number of Baffles: 34
Baffle Spacing: 0.05 m

Sketch



Shell & Tube Heat Exchanger

Shell			**Tube**		
Cooling Water Set Flowrate:	90.4	kmol/hr	Gas Mixture Flowrate:	2.04	kmol/hr
Cooling Water Inlet Temperature:	20.0	°C	Gas Mixture Inlet Temperature:	370	°C
Cooling Water Outlet Temperature:	30.0	°C	Gas Mixture Outlet Temperature:	30	°C
Phase Change:	None		Phase Change:	Condensation	
Operating Pressure:	14.7	psia	Operating Pressure:	200	psia

Overall Heat Transfer Coefficient: 500 W/m^2-K
Heat Transfer Area: 0.42 m^2
Material of Construction: SS-304

***Note: Flowrates are on a per module molar basis**

W-411	STORAGE TANK SPECIFICATION SHEET	Page 1 of 1

Number of Units Per Module: 1
Number of Modules: 60
Total Units: 60
Plant Section: 400 - Storage & Energy

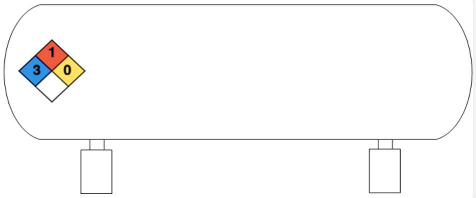
Design Pressure: 250 psig
Operating Pressure: 200 psia
Weld Examination: Fully Radiographed, Double-welded butt joint
Joint Efficiency: 85 %
Corrosion Allowance: 2.0 mm
Wall Thickness: 7.5 mm

Operating Temperature: 25 °C

Materials of Construction: SS-304

Shell Diameter: 0.75 m
Shell Length: 3.74 m
Shell Mass: 123 kg

Sketch



Pressurized Anhydrous Ammonia Storage Tank

X. Equipment Cost Summary

Equipment #	Key Dimension	Total # of Units	Costing Method(s)	FOAK Cost (2020)	Total Cost (2020)
Starting Medium	N/A	N/A	Quote per chemical	N/A	$1,070,000,000
PBR Piping	N/A	N/A	PVC Quote	N/A	$17,143,005,000
C-111	N/A	11,400	Picked value in observed range	$10,000	$114,000,000
Greenhouse Infrastructure	H = 7.8 m, L = 488.8 m	60	Quote per sqft Polycarbonate	$691,500	$41,487,000
P-110	Flow = 459 L/s	1714740	Peters and Timmerhaus, Towler	$32,820	$56,274,300,000

De-ionizer	N/A	1	Quote (Alibaba)	$62,500	$62,500
Fluorescent Lights	L = 10888.6 m per module	506400	Quote (Alibaba)	$1.63	$873,500
M-210	Surface Area = 2287.5 m^2	60	Empirical Data ($16/m^2)[40]	$36,600	$836,700
T-210	Volume = 1660 m^3	60	Peter and Timmerhaus [43]	$513,100	$11,733,000
H-211	Surface Area = 202.5 m^2	60	Peter and Timmerhaus	$58,870	$1,346,200
H-212	Surface Area = 4185 m^2	60	Peter and Timmerhaus	$506,400	$11,580,000
B-211	Steam Flowrate = 150000 kg/hr	60	Towler and Sinnot [44]	$2,730,000	$62,429,000
C-211	N/A	60	Picked value in observed range	$10,000	$228,700
C-212	N/A	60	Picked value in observed range	$10,000	$228,700
X-311	Duty = 343 kW	60	Towler	$11,850	$271,000
H-312	Area = 24.8 m^2	60	Towler	$34,400	$786,000
A-310/320/ 330/340	Tube surface area = 0.27 m^3	240	Woods' Power Law	$67,050	$6,821,500
A-310/320/ 330/340	Absorbent mass = 66.8 kg	240	Woods' Power Law	$54	$12,970
H-313	Area = 2.08 m^2	60	Towler	$6,500	$148,600
X-314	Duty = 7.1 kW	60	Towler	$5,310	$121,500
H-315	Area = 0.42 m^2	60	Towler	$3,000	$68,600
T-411	Shell mass = 600 kg	60	Towler	$40,000	$887,000

W-410	Power Rating = 3 MW	31,682	NREL & GE Cost Estimates	$2,200,000	$69,777,400,000
W-412	Storage Capacity = 1 MW	63,434	NREL 2019 Cost Estimates	$1,880,000	$119,255,900,000
				Miscellaneous	$7,473,000
				Lang Factor	**1.7**
				Total Cost	**$461,100,000,000**

Note: The vacuum pump for recycling air (T-316) was factored in under miscellaneous costs, along with valves, instrumentation, and other minor equipment. Miscellaneous costs were assumed to be 10% of the total equipment costs (omitting energy infrastructure).

The following table summarizes the parameters used to estimate capital costs with the Towler Correlation ($C = a + bS^n$).

	a	**b**	**n**
Pump	8000	240	0.9
Compressor	4450	57	0.8
Heat Exchanger	1900	2500	1

First of a kind (FOAK) costs for each piece of equipment were calculated through various correlations used for traditional stick-built plants. Some pieces of equipment were outside the size ranges used for correlations and in these cases, quotes were obtained or correlations were extrapolated as a conservative estimate. For each consecutive unit produced, an economy of mass production scale was used through the following equations:

$$k_n = k_1 n^{\log_2(p)}$$

$$K(N) = \sum_{n=1}^{N} k_n$$

Where, k_1 is the FOAK cost, k_n is the cost of the nth unit, p is one minus the learning rate, and *K(N)* is the total cost of N units. For modular manufacturing, it was assumed that the learning rate was 20%, such that the unit module cost decreased by 20% every time the production quantity doubled. This yielded a p value of 0.8. An example of the curve that results from this relation is shown in the following plot, based on Equipment C-414.

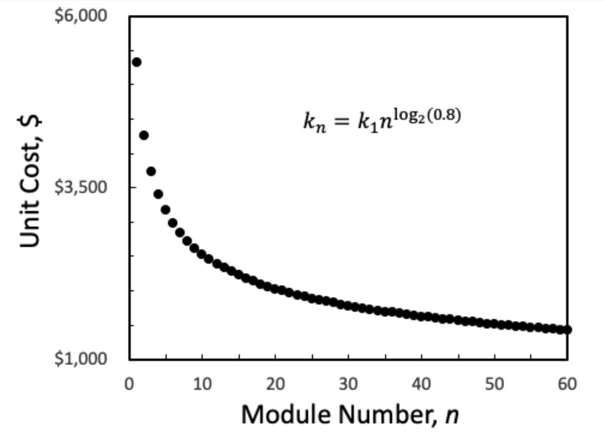


Figure 10.1. Cost for each consecutive unit for the compressor C-414. Each piece of equipment follows the same curve, however with differing FOAK costs (k_1). With every doubling of production quantity, the unit module cost decreases by 20%.

More details on the capital equipment cost estimation procedures is provided in the Appendix.

XI. Fixed Capital Investment Summary

Commented [CH1]: actions to reduce cost

In summary, results from the previous section provided a total installed cost of $461B for the plant. The following pie charts summarize the primary sources of such a high capital cost.

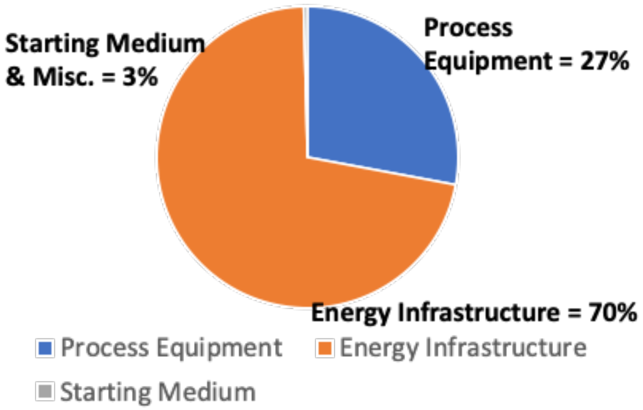


Figure 11.1. Fixed capital investment breakdown. The energy infrastructure is the most significant cost driver of the CAPEX at 70%, while process equipment makes up 27% and the starting culture medium and miscellaneous costs make up 3% of the installed cost.

On further inspection, the photobioreactors and pumps made up 23% and 76% of the process equipment costs (omitting energy infrastructure and starting raw materials). To obtain a better picture of the cost breakdown, without including the major cost drivers, another pie chart is shown below.

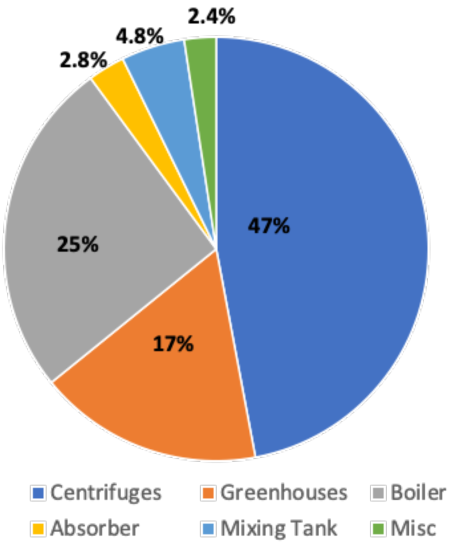


Figure 11.2. Cost breakdown of process equipment, omitting the photobioreactors and pumps. The centrifuges, greenhouses (which make up a module), and boiler make up the majority of minor process equipment costs.

Further economic analysis of the capital costs, as well as overall profitability of the plant, is provided in Section 13.

XII. Manufacturing/Operation Costs

Operating Labor

Operating labor costs were primarily based on an estimated number of operators for each piece of equipment in the plant. It was assumed that operators had a yearly salary of $60,000, which is typical for equipment operators in Minnesota, and that there were five crews of operators to account for time off and varying shift lengths. The following table summarizes some assumed operator requirements for various process equipment in the plant.

Equipment Type	Operators per Unit per Shift
Pumps	0
Heat exchanger	0.1
Blowers and compressors	0.1

Boilers	1.0

Since these recommended operator requirements did not include membranes and photobioreactors, some further assumptions were made. The membranes and photobioreactors are highly passive in their operation. Auxiliary pumps and centrifuges for the photobioreactors were assumed to require some operator oversight. It was concluded that a reasonable estimation was one operator per section per module, or a total of 3 operators per module (1 for the photobioreactor section, 1 for the membrane section, and 1 for the purification section). This was a total of 180 operators per shift. Using an assumed 5 crews, this was 900 total operators for the plant. Such a large operator requirement is necessary due to the large number of parallel modules used in the plant. This number of modules was based on the required medium and culture flowrates to the centrifuges in the photobioreactor section. The required centrifuge size was not feasible at a lower number of modules, as this would have required a larger flowrate duty for each centrifuge. Again, an improved photobioreactor production rate would allow for lower flowrates and thus lower overall costs of the plant, however further pilot-scale research on genetically modified photobioreactors is required to determine the feasibility of obtaining a higher production rate.

The total operating labor costs are:

$$Operating\ Labor = OL = (\#\ operators\ per\ crew)(\#\ crews)\left(\frac{\$60000}{yr}\right)$$

$$OL = (180)(5)\left(\frac{\$60000}{yr}\right) = \mathbf{\$54,000,000 = \$54}\boldsymbol{M/yr}$$

Yearly labor related costs, which account for employee benefits such as insurance and other expenses, can be calculated using a rule of thumb that they are 60% of the yearly operating labor costs.

$$Labor\ Related = LR = 0.6(OL) = 0.6(\$54M) = \mathbf{\$32.4}\boldsymbol{M}$$

Utilities and Raw Materials

HX-212 Cooling Water:
The molar flow rate through HX-212 was calculated to be 349000 kgmol/hr. This can be converted to an operating cost, assuming a cost for cooling water. Assuming cooling water costs \$10 per 1000 m^3, as per the plant design project specified from last term, the final operating cost of HX-212 can be calculated.

$$OC = 349000\frac{kgmol}{hr} * \frac{18.02\ kg}{kgmol} * \frac{1\ m^3}{1000\ kg} * \frac{\$10}{1000\ m^3} = \frac{\$62.89}{hr}$$

So, it costs about \$62.89 per hour to run HX-212. Since there are 60 modules, it takes 60*\$62.89 per hour to run the HX for the whole plant. This corresponds to an hourly cooling water cost of \$3773.4 per hour, or a yearly cost of \$3,310,000 per

Energy requirements from the pumps totaled 5045294 MW, an extreme energy requirement that can be attributed to the high velocity and consequent friction losses of the culture medium as it flows through the photobioreactors. To maintain a carbon-neutral plant, the total CO_2 consumed in the plant was estimated, and then the natural gas CO_2 emissions were set equivalent to that, with the rest of the energy requirements for the pumps being met by wind turbines. At an assumed 1.5% CO_2 in air bubbling through the photobioreactors, and an air flowrate of 119174 m^3/min, the yearly CO_2 consumption was calculated as follows:

$$\left(119174\frac{m^3\ air}{min}\right)\left(0.015\frac{CO_2}{air}\right)\left(60\frac{min}{hr}\right)\left(24\frac{hr}{day}\right)\left(365\frac{day}{yr}\right)\left(1.98\frac{kgCO_2}{m^3}\right)$$
$$= \mathbf{1.86x10^9\frac{kgCO_2}{yr}\ consumed}$$

Department of energy sources suggested the CO_2 emissions rate for natural gas was 53.07 kg/MBTU. If the pump energy requirements were met entirely by natural gas, the following CO_2 would be emitted per Joule of energy.

$$\left(53.07\frac{kg}{MBTU}\right)\left(\frac{1\ BTU}{1055.06\ J}\right)\left(1\frac{MJ}{10^6 J}\right) = 5.03x10^{-8}\frac{kg}{J}$$

Furthermore, the yearly pump requirement was:

$$(5045294\ MW)(10^6)\left(3600\frac{s}{hr}\right)\left(24\frac{hr}{day}\right)\left(365\frac{day}{yr}\right) = 1.59x10^{20}\frac{J}{yr}$$

The yearly natural gas CO_2 emissions were set to the CO_2 consumption rate, and an Excel solver was used to back out the total allowable pump energy covered by natural gas. In Excel, this yielded $3.7\text{x}10^{16}$ J/yr covered by natural gas. This meant a remaining 95,047 MW had to be covered by the wind turbines. Using 3 MW wind turbines, this was a total of 31682 wind turbines for the pumps. Compression and heating requirements for the steam boiler and absorber are derived from the wind turbines, and thus have no direct utility costs. The boiler had an 81 MW duty, the compressors had a 21 MW duty, the fluorescent lights had a 1.8 MW electric duty (assuming 14 W per 4 ft bulb), and the absorbers had around 0.5 MW heating duty. This was a total energy requirement of 104 MW, which required an additional 35 three-MW wind turbines. In total, 31717 three-MW wind turbines were required to meet the energy requirements of the plant. This is clearly unrealistic as it would take up a significant land mass and capital cost, however as currently designed these figures will be used in the economic analysis of the plant. It would work in theory, however not in reality.

Maintenance & Sales-Related Costs

Yearly maintenance and equipment upgrade costs, summarized as a capital-related expense, are assumed to be 26% of the initial CAPEX.

$$Capital - related = CR = 0.26(CAPEX) = 0.26(\$461) = \$\$120B/yr$$

The yearly sales of the plant must be calculated to obtain the sales-related costs, which are assumed to be 20% of the yearly sales. A 25% profit margin was assumed, and the following equation can be used to determine the total sales, where PM is profit margin, R is raw materials, U is utilities, OL is operating labor, LR is labor related, CR is capital related, and S is sales.

$$S\ = (1 + PM)(R + U + OL + LR + CR + 0.2S)$$

$$S = \frac{R + U + OL + LR + CR}{0.8 - 0.2PM}$$

$$S \ = \frac{\$2.79B + \$0.17B + \$0.054B + \$0.032B + \$120B}{0.8 - 0.2(0.25)} = \$163.9B/yr$$

Thus, sales related costs (SR) are:

$$SR = 0.2S = 0.2/yr) \quad = \$32.8B/yr$$

XIII. Economic Analysis

Going off the yearly sales calculated in the previous section, a unit sales price for the ammonia product can be calculated based on the 25% profit margin and yearly production rate.

$$Unit\ Sales = \frac{S}{(50\ mtpd)\left(365\frac{day}{yr}\right)\left(1000\frac{kg}{metric\ ton}\right)} = \frac{\$163.9B/yr}{18250000\frac{kg}{yr}}$$

$$Unit\ Sales = \frac{\$\,8{,}981/kg}{kg\ of\ Ammonia\ produced}$$

To put this in perspective, the current market price of ammonia is estimated as \$512/ton, or \$0.52/kg. From this key performance indicator alone, it is clear the plant would not be competitive or profitable. Manufacturing costs would have to decrease by a factor of 17,500 to be market-competitive.

To further analyze economic costs and profitability of the plant, the following pie charts break down the major cost drivers of the plant's manufacturing costs, utilities, and capital costs.

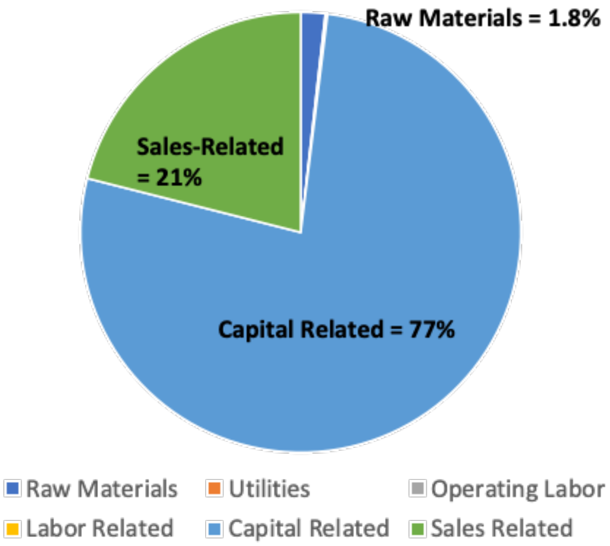


Figure 13.1. Breakdown of yearly manufacturing costs. Sales-related costs are 21%, raw materials are 1.8%, capital-related costs are 77%, and utilities, operating labor, and labor-related costs make up the difference.

As Figure 1 shows, the yearly manufacturing costs are driven by the significant capital cost, which created a large portion of yearly maintenance costs. If the capital-related and sales-related costs were ignored, the majority of the operational costs would be from raw materials (i.e. replenishing the culture medium).

DCFROR (or IRR) and NPV are other key profitability metrics, and the following 5-year MACRS schedule over a 20-year plant life reflects the yearly cash flow and present value, which is then converted to an overall NPV and an IRR. The 5-year MACRS depreciation schedule was obtained from *IRS Publication 946, Table A-1*. The gross profit is calculated as follows:

$$Gross\ profit = Sales - Manufacturing\ Cost$$

Furthermore, the depreciation charge each year is calculated as follows:

$$Depreciation\ charge\ in\ year\ n = (CAPEX)(Depreciation\ Rate\ in\ Year\ n)$$

The yearly taxable income was calculated by taking the difference of the gross profit and the depreciation charge.

$$Taxable\ Income = Gross\ Profit - Depreciation\ Charge$$

Using a corporate tax rate of 21%, the taxes paid are calculated for the following year.

$$Taxes\ Paid\ (in\ year\ n + 1) = 0.21 * (Taxable\ income\ in\ year\ n)$$

The cash flow is calculated by taking the gross profit in year n and subtracting both the capital investment in that year and the taxes paid. Since capital related expenses were already accounted for in manufacturing costs, the yearly capital investment is $0. Thus, the cash flow is:

$$Cash\ flow\ =\ Gross\ profit - Taxes\ Paid$$

Each year, the present value of the plant can be calculated:

$$Present\ value = P = \frac{CF}{(1+i)^n}$$

This calculation was conducted each year over the 20-year period, and the net present value (NPV) and IRR were calculated as follows:

$$NPV = \sum_{n=1}^{n=N} \frac{CF_n}{(1+i)^n}$$

$$IRR: \sum_{n=1}^{n=N} \frac{CF_n}{(1+i')^n} = 0, solver\ used\ to\ obtain\ i'(the\ IRR)$$

The following table summarizes all these calculations over the 20-year plant life (in billions of dollars).

Year	CAPEX	Gross Profit	Depreciation %	D-Charge	Taxable Income	Taxes Paid	CF	Present Value
0	$461B	-	0	-	-	-	-$461B	-$461B
1	-	$8.2B	20	$92.2B	-$84B	-$18B	$8.2B	$7.3B
2	-	$8.2B	32	$148B	-$139B	-$29B	$25.8B	$20.6B
3	-	$8.2B	19.2	$88.5B	$80B	-$17B	$37.5B	$26.6B
4	-	$8.2B	11.52	$53.1B	-$45B	-$9.4B	$25.1B	$15.9B
5	-	$8.2B	11.52	$55.1B	-$45B	-$9.4B	$17.6B	$10.0B
6	-	$8.2B	5.76	$26.6B	-$18B	-$3.9B	$17.6B	$8.9B
7	-	$8.2B	0	-	$8.2B	$1.7B	$12.1B	$5.5B
8	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$2.6B
9	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$2.3B
10	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$2.1B
11	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$1.9B
12	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$1.7B
13	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$1.5B
14	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$1.3B
15	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$1.2B
16	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$1.1B
17	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$0.94B
18	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$0.84B
19	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$0.75B
20	-	$8.2B	0	-	$8.2B	$1.7B	$6.5B	$0.67B
							NPV	-$347B
							IRR	-7.6%

This analysis suggests the plant, as currently designed, is not profitable, and would be a net loss of $347 billion. An IRR of 8% was the target metric for profitability, and not meeting this suggests the plant should not proceed with construction or further design. Further sensitivity analysis and discussion on how the plant could be profitable is provided below and in the Conclusions and Recommendations. Finally, the payback period of the plant can be calculated as follows:

$$Payback\ Period = \frac{Initial\ Investment}{Gross\ Profit}$$

$$Payback\ Period = \frac{\$461B}{\$8.195B} = 56\ years$$

This is a significant time period, and it is unlikely the plant could sustain such a long operational lifetime. Thus, it is concluded that it would be risky to make such a large investment without first exploring designs that could prove to be more profitable for small-scale ammonia production. To further analyze the plant's key drivers for profitability, sensitivity studies on the production volume, CAPEX, raw materials price (feedstock), and utilities. For production volume, the capital cost was scaled by the following modular manufacturing mass production equation:

$$k_2 = k_1(1 + n^{\log_2(p)})$$

Where, k_2 is the new cost, k_1 is the original cost, n is the ratio of the new number of modules to the old number of modules, and p is a production constant of 0.8. Figures relating the sensitivities of each of these parameters to the unit sales price, NPV, and the IRR are shown below.

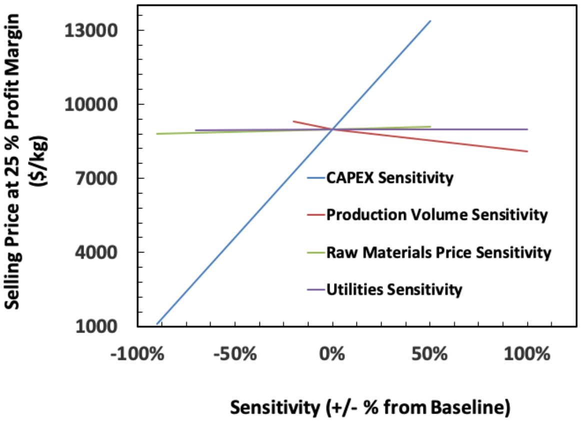


Figure 13.2 – Sensitivity analysis of capital cost, production volume, raw materials price, and utilities and their impact on the unit sales price at a 25% profit margin.

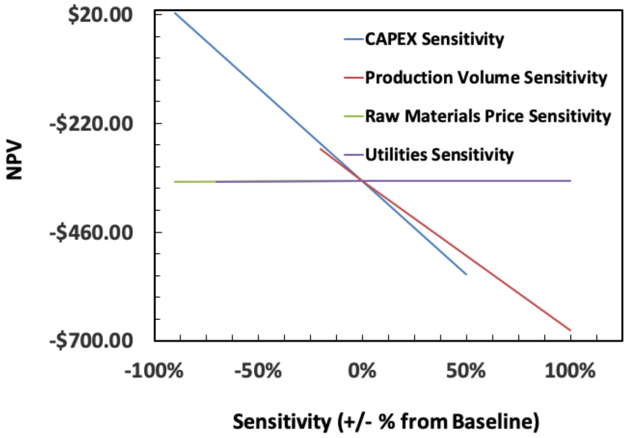


Figure 13.3 - Sensitivity analysis of capital cost, production volume, raw materials price, and utilities and their impact on net present value at a 25% profit margin. Capital cost and production volume are the biggest cost drivers of the plant, and a 90% decrease in capital cost would provide a positive NPV, as desired. NPV is listed in billions of dollars (USD).

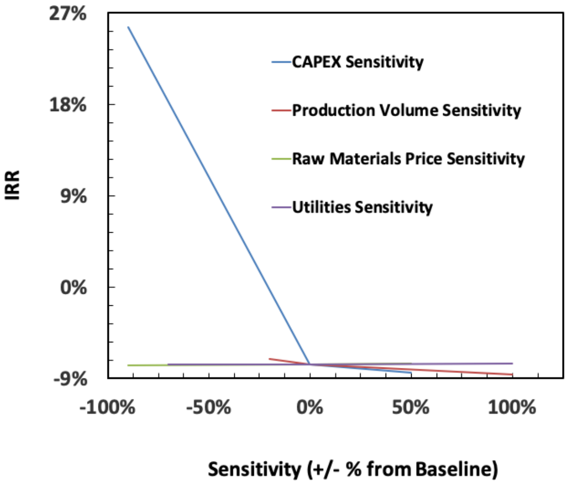


Figure 13.4 – Sensitivity analysis of capital cost, production volume, raw materials price, and utilities and their impact on the discounted cash flow rate of return (DCFROR). The most optimal method for improving IRR and meeting the target 8% is to find methods for decreasing the plant's capital cost.

The primary cost drivers of the unit sales price or DCFROR are indicated by the steepest lines in these sensitivity charts. The conclusion of these is that capital cost is the most significant cost driver of the plant. Production volume is another key performance indicator for the plant's profitability, as shown by its steel slope in the Figure 3 (DCFROR). Exploring methods to decrease the required flowrate of the culture medium would significantly improve capital and operating costs, and could ultimately shift the plant towards profitability.

Another important metric is the relationship between the number of modules, the cost per module, and the total cost based on the number of modules. The intersection of these curves is indicative of the most economically-optimal number of parallel modules in the plant. The following graph shows the cost per module on one axis, and the sum of the costs for *n* modules on the secondary axis.

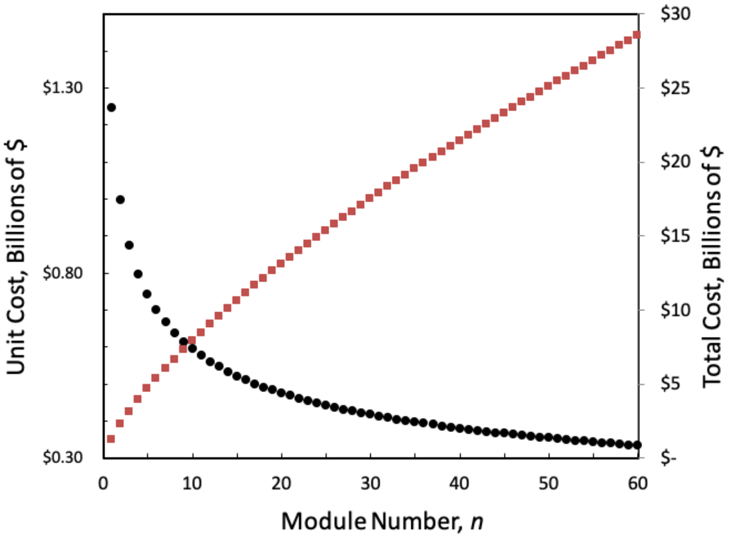


Figure 13.5 – Relationship between cost per module and total costs for *n* modules. At the intersection, the costs are theoretically optimized under a fixed-cost model.

Figure 13.5 suggests the optimal number of modules for this design is 9, and after that diminishing returns are seen as the number of modules increases. However, this is a fixed-cost model, and a variable-cost model would more accurately optimize the number of modules by accounting for the changing flowrates in the photobioreactors, which largely dictate the pump sizes. At a lower number of modules, the flowrate is very high and turbulent, meaning frictional losses create an extreme energy duty for the pumps. However, a higher number of modules decreases the flowrate, which consequently decreases the pump duties. So, it is more realistic to increase the number of modules in search of a more profitable plant in this case, although Figure

3 provides an adequate sense of the optimal number of modules for more traditional ammonia production processes that aren't as reliant on liquid flowrates.

Finally, the required production rate of cyanobacteria to allow for a profitable plant was calculated as follows.

Currently, as this plant is entirely experimental, and these processes have never been scaled up to this size before, the fact that this plant is so unprofitability is hardly a surprise. However, it is worth taking a short look at what changes might allow this plant design to turn a profit. As shown in Figure 13.4 the profitability of the plan is most dependent on the capital cost. Any way to lower the capital cost of the plant could deliver large gains in changing the profitability of this plant. For this plant to turn a profit, it would need to reduce its capital cost by at least 90%, according to Figure 13.3.

Much of the capital equipment is so expensive just based on the required scale of the plant. Requiring a fluid volume of over 2.3 million cubic meters and a land area of over 1000 acres is the largest contributor to these absurd capital costs. Many of the most expensive pieces of capital, such as the bioreactor and greenhouses, have costs that scale directly with the required volume of fluid. Additionally, the sheer number of pumps and centrifuges, as well as the size of required heat exchangers, are all also influenced by the fluid volume. These are the main source of power requirements, and the price of the wind turbines are singlehandedly the largest component of the plant capital cost.

The crux of the issue is that the cyanobacteria are not productive enough to make any equipment make sense on the scale required to produce 50 mptd of ammonia. If the bacteria could be more productive in a given unit volume, that could lead to incredible leaps to reducing the required volume of the plant, drastically reducing capital costs. If the cyanobacteria could have their productivity increased 10 fold in a unit volume, through a combination of creating cyanobacteria that can produce more ammonia or can operate in higher cell densities, the required fluid volume for the plant would be reduced to 1/10th the calculated size. Since most of the largest capital and operating costs scale relatively linearly with the volume of fluid required, this would also represent a transition to a plant that requires roughly 1/10th of the capital cost. This is also a 90% decrease in capital cost, which would bring the plant onto the brink of profitability.

Since this plat is highly experimental, and these processes have never been implemented on an industrial scale before, it is expected that the lab-scale data has not been optimized for industrial performance. An increase in cell productivity of 10-fold would be difficult, but it does seem possible. Research on cyanobacteria and algae has been sparse in recent times because it is generally explored as methods for alternative energy and fuel source, and oil has been cheap in recent years. This fact that cyanobacteria are not heavily studied, especially in these sorts of applications, makes a large leap in productivity more likely. So, while a 10-fold increase in production rate per unit volume is ambitious, it is not outside the realm of possibility. Therefore, it seems like the most likely way to make an industrial ammonia plant like this become profitable in the future is to research cyanobacteria to increase their productivity, either via genetic engineering or shifting environmental factors.

XIV. Safety, Health, and Environmental Considerations

Safety

The Center for Chemical Process Safety (CCPS) Process Safety Pillar "Learn from Experience" was the emphasis of safety analysis for this plant. "The AIChE Ammonia Safety Symposium: 50 Years of Shared Experiences" provided a summary of many incidents that occurred worldwide in ammonia plants up until 2001. Although many incidents were related to the traditional Haber-Bosch process and production of H_2 and N_2 feedstock gases, some insight was gained for improving heat exchanger, compressor, and storage tank design in this novel modular ammonia production plant. Methods to prevent recurrence of these incidents were implemented in the form of control systems or clear recommendations and guidelines for construction & operational inspections.

Some notable and relevant incidents include a fatality in 2001 when a contractor fell through a plastic skylight outside a taped work area; a fatal suffocation in a CO shift convertor; a brittle fracture on the dished end of a bulleted pressure storage tank; an explosion of an NH_3 separator due to the buildup of mercury; a high pH level caused damage to a boiler; a NH_3 loading line ruptured and released 180 tons of ammonia; a reverse flow phenomena caused ingress of process gas into a storage tank and sparked an explosion; a storage tank overflow occurred in Blair, Nebraska on 16 November 1970 due to a failure of the high level alarm; a storage tank partially collapsed due to a vacuum that developed from the failure of a pressure transmitter after a power outage; damage to a storage tank's foundation resulted from ground movement; and, stress corrosion on a storage tank resulted from on-site weld procedures that produced microstructures with a tendency to crack. Many of these can be avoided in the modular plant design by implementing safeguards based on the CCPS "Learn from Experience" pillar. The following table summarizes these relevant incidents in the history of ammonia production, and provides a description of the action implemented into the design of this novel plant.

Incident	Cause	Design Improvement
Fatal fall through skylight.	Worker was outside taped work area, possibly undertrained.	Provide harnesses for elevated work and implement barricades for work areas rather than taping them off.
Fatal suffocation in CO shift convertor.	Unauthorized confined space entry.	Implement stringent confined space entry requirements and mandate annual training.
Brittle fracture on pressure storage tank caused 30 tons of NH_3 release & 18 deaths at AE&CI Ltd, Potchefstroom, South Africa plant.	Vessel not stress-relieved after manufacturing & strain aging weakened the structure.	Stress-relieve key vessels after manufacturing and conduct inspections.
Explosion of NH_3 separator.	Build-up of 10 kg mercury in separator, which forms explosive compounds with steel.	Installed mercury composition analyzers on feeds to vessels, and

Damage to boiler.	High pH level.	Material compatibilities were analyzed for the plant sections with high pH levels.
Loading line rupture caused release of 180 tons of ammonia.	Hydrolysis of ammonia in an incompatible polyester hose.	Material compatibilities were analyzed for all possible components & design decisions were made accordingly.
Storage tank explosion.	Start-up conditions caused process gas ingress into storage tank.	Check valves were installed on the storage tanks to ensure reverse flow does not occur.
Storage tank overflow.	High level alarm and shutdown system failure.	Vessels were equipped with overflow systems including a relief valve and block valve. Secondary level indications were implemented on storage tanks.
Storage tank partial collapse.	Vacuum resulted from failure of pressure transmitter after power outage.	An additional pressure indicator was installed on storage tanks.
Storage tank foundation damage.	Earthquake combined with freezing and thawing of ground.	It is recommended that foundation be water-proofed. The chosen plant location is also not susceptible to earthquakes.
Stress corrosion on tank.	On-site weld procedures did not follow the correct standards.	Cleats are recommended to be installed on the outside of tanks, and stringent weld procedures should be implemented.
Localized heat exchanger corrosion.	Welding inadequacies and incompatible bolts.	Corrosion allowance (minimum 2 mm) has been implemented into the wall thickness of all equipment; corrosion-resistant coatings are recommended during design as well.
Waste heat boiler failures.	Defects introduced during manufacturing or fabrication.	Modular plant allows for less-specialized manufacturing (larger production quantity for each equipment part). It is recommended that all equipment be inspected during and after fabrication.
Downstream failure of waste heat boiler.	Sludge deposits from chemical cleaning.	Install blowdown on heat exchanger liquids.

Leaking of ammonia into annular space of double-integrity ammonia storage tank.	Level alarm high did not trigger.	Parallel recording instruments for level control in the annular section of storage tanks were implemented. Indicators were changed to fail-safe, and it is recommended an interlock be installed to trip ammonia pumps if annulus levels reach above a 400 mm level.

Since many incidents were caused by issues introduced in the manufacturing and operation of the plant, it is difficult to properly address them in early design stages. To address concerns related to inadequacies in construction and operational maintenance, the following guidelines are recommended during the construction process and the plant's operational life-time:

Safety Recommendations During Plant Start-up and Operation

1. Conduct spot-radiographic examinations on all welded joints.
    a. For storage tanks and heat exchangers, conduct full radiographic examinations on welded joints.
2. Install blow-downs on cooling water streams (heat exchangers) to prevent build-up of solids and blocked inlets/outlets.
3. Provide stringent training and Standard Operating Procedures for confined space entry.
    a. Ensure all operators are trained and re-trained annually, respirators are available on-site, and that composition analyzers are available and used prior to entering a confined space. If possible, purge chambers with air prior to confined space entry.
4. Obtain expert advice and detailed design work from mechanical and electrical engineers when designing specifics for compressors and pumps. Specifically, ensure shrouds and blading are designed to handle the stresses of the air flowrates.
5. For all maintenance work, ensure work areas are barricaded, notices are sent to all employees so they are aware of the work, and that at least two specially-trained employees are present.
    a. For any maintenance requiring elevation, mandate the use of harneses.
6. Update all documents, SOPs, and specification sheets to "as built" operating conditions and designs to prevent confusion and streamline root cause analysis for any incidents or problems that do occur.
7. If a power outage occurs, examine all control systems (i.e. transmitters) during the start-up of the plant to ensure everything is working properly.
8. Install a composition analyzer on streams entering storage tanks or other vessels to monitor mercury levels. Although unlikely to be present in appreciable amounts, mercury can change steel properties and create explosive compounds.
9. Inspect heat treatment and final steel properties during fabrication to ensure steel is austenitic rather than bainitic (brittle).
10. Implement acoustic emission testing both during start-up and on an annual basis to ensure the plant is within reasonable noise levels. During construction, install acoustical insulation, barriers, and energy absorption devices around the plant to minimize noise

levels. Provide ear protection to all employees and provide clear signage indicating locations where ear protection is required.

Additional safety considerations were suggested by the Ammonia Safety Symposium report. Specifically, the use of a Distributed Computer Control System (DCS) is recommended for the plant rather than pneumatic control systems. This is reflected in the P&ID in Section VIII of this report. DCS provides a more consistent and smooth operation, and furthermore has the ability to produce process logs that are easily accessible for operators and engineers to monitor the performance of the plant and note any anomalies that could be indicative of a future safety issue. The use of an advanced control system only serves to benefit the plant, despite higher costs typically associated with more advanced systems. A less sophisticated control system could result in a serious incident that would cost the plant much more than an advanced control system that could have detected and mitigated such an incident. Redundancies in control systems are another factor that should be implemented throughout the plant. More detailed safety analyses should be conducted by individuals and experts from many different backgrounds to ensure nearly all hazards have been considered and mitigated prior to construction of the plant.

Since the as-designed plant does not use the traditional Haber-Bosch process, and instead uses a photobioreactor system, further research was conducted to identify past incidents in photobioreactors and to thoroughly address the “Learning from Experience” pillar of CCPS guidelines. One incident at a UC Berkeley lab involved over pressurization of a glass bioreactor and led to injuries for one individual. Although not an industrial incident, over pressurization is a concern in this plant due to the significant water volume and gas sparging through the photobioreactors. A design decision was made to use plastic for the photobioreactors, which can often be processed to withstand high pressures and does not shatter the same as glass. Furthermore, it is recommended that special consideration be given to the initial scale-up of the culture and production of the medium, which may contain toxic chemicals.

Although “Learning from Experience” was the focus of this safety analysis, the CCPS “Guidelines for Risk Based Process Safety” goes in depth on other safety pillars such as “Commitment to Process Safety,” “Understand Hazards and Risk,” and “Managing Risk.” To be thorough, the following table provides some brief recommendations for each of these pillars to ensure the plant will have minimal incidents in its process lifetime.

Pillar	Design Recommendations and Action Items
1st Pillar: Commitment to Process Safety	• Establish a process safety culture through extensive training for operators, frequent re-trainings, and by rewarding employees that meet and exceed safety standards. • Have an active EHS department that encourages reporting of safety incidents or near misses and works to prevent recurrence of safety problems. Ensure EHS department monitors compliance standards and works to adjust plant processes as necessary. • Reach out to the community near the plant to gather suggestions or complaints regarding the plant.

	• Include all employees in review of safety incidents or near misses, including those that occur at other plants in the chemical industry but may be relevant to our plant.
2nd Pillar: Understand Hazards and Risk	• Conduct HAZOPs and other safety analysis methods with experienced professionals, operators, entry-level engineers, and other stakeholders that could provide valuable insight into identifying and minimizing hazards and risks. • Use hazard and risk information to plan, develop, and deploy operations that are lower risk.
3rd Pillar: Managing Risk	• Maintain updated and accessible operating procedures for all plant processes and equipment. • Ensure contractors receive the same training as permanent plant employees. • Manage changes to processes by conducting detailed safety analyses and ensuring risk remains tolerable for all changes. • Maintain well-established emergency and containment plans in case an incident does occur.
4th Pillar: Learning From Experience	See tables and discussion above.

More information on specific process safety considerations for this plant is provided in Section XVI.

Health

To determine the health hazards that the plant presents to both its employees and the public, a list of all chemicals involved in the plant was compiled along with their SDS information. Mitigation steps were based on SDS suggestions and typical industry health precautions. Additional health hazards, such as UV light exposure, are presented in the table along with the chemical hazards.

Table 1. Assessment and mitigation of potential health impacts associated with the ammonia production plant.

Chemical or Hazard	Associated Health Risks	Mitigation Steps
Ammonia, NH_3	Eye damage, severe burns, harmful if inhaled, causes suffocation if oxygen is displaced. Toxic to aquatic life.	Secure storage vessels and ensure adequately rated pressure. Use adequate ventilation and keep gas vapor below lower explosive limits. Provide necessary PPE and confined space training for employees, use compatible material for equipment (Stainless Steel 304 is compatible). Use BACT practices to monitor ammonia levels in waste streams, and to treat streams appropriately.
Water, H_2O	None associated.	Use composition analyzers to determine other chemicals dissolved

		in water, and use BACT practices for waste treatment and disposal.
Air, *N_2 & O_2*	Frostbite from rapid expansion.	Pressure and temperature sensors/transmitters available at the inlet/outlet of vessels and pumps or compressors. Routine inspections to ensure piping has not corroded and no leaks are present.
Pure Nitrogen, *N_2*	Asphyxiation Frostbite from rapid expansion.	Provide all employees with confined space training. Monitor nitrogen composition levels to take appropriate actions if maintenance on a vessel is required. Provide ventilation to prevent displacement of oxygen on the plant floor in case of nitrogen leak.
Sulfuric acid, *H_2SO_4*	Severe corrosion resulting in skin burns & eye damage, nausea/abdominal pain if ingested, acute and chronic respiratory problems.	Provide exhaust ventilation and ensure emergency eye wash stations are nearby vessels and piping containing sulfuric acid. Use stainless steel as a compatible material to avoid corrosion and exposure. Ensure employees have butyl rubber, polyethylene, or tetrafluoroethylene gloves and PPE, as well as a type E gas mask on hand. Place sulfuric acid detectors on the plant floor to alarm for evacuation in case of emergency.
Carbon dioxide, *CO_2*	Frostbite from rapid expansion, asphyxiation if oxygen is displaced. Can decompose under heat to carbon monoxide.	Design vessels for proper pressure rating and stress test. Provide all employees with PPE such as respirators, ensure adequate ventilation for the plant.
Carbon monoxide, *CO*	Toxic if inhaled, toxic to reproduction, can cause chronic organ damage.	CO detectors placed both on vessels and around the plant floor to allow for evacuation if levels rise above 25 ppm. Ensure enough respirators are on-site for all employees. Engineering controls: ventilation, thermal sensors to ensure CO_2 is not at temperatures conducive to degradation.
Sodium Alginate, *NaAlg*	Ingestion may cause gastrointestinal irritation.	Ensure adequate ventilation and maintain in solution to prevent airborne dust or mist contamination.

Chlorophyll	Acute redness and burning of skin and eyes, irritation of mucus membranes if ingested.	Ventilation, chemical resistant PPE, respirators available and eyewash facility/safety shower on plant floor.
Lithium ion battery packs	Cell electrolyte can cause skin/eye irritation or chemical burns. Can cause severe respiratory irritation if inhaled or ingested. Electric shock could result from high voltages.	Store batteries in a blocked off area of the plant. Ensure barricades are up at all times, and employees are properly trained to conduct maintenance on batteries. Regularly inspect the cooling system to ensure overheating or leaks do not occur.
Anabaena variabilis	Can produce anatoxin and microcystin toxins, causing liver damage or acute abdominal pain if ingested.	Monitor waste streams for anabaena variabilis concentrations and use BACT practices to properly treat waste before being returned to the environment. Monitor toxicity levels of algal blooms in the bioreactors and ensure employees have relevant biohazard training.
Chlorella vulgaris	Side effects can include nausea and gastrointestinal problems if large amounts are ingested.	Provide proper ventilation and ensure employees have relevant training and PPE.
UV Light	Long-term exposure can cause skin cancer, skin damage, eye damage/cataracts, and possible immune system suppression.	Provide eye protection and require UV-protective clothing for all employees working on the plant floor.
Warm temperatures in greenhouses	Can lead to dehydration and heat stroke.	Provide employees with sufficient breaks in air-conditioned rooms and free water. Heat the photobioreactors internally and implement temperature sensors to monitor changes.
Loud and persistent noises	Hearing loss, tinnitus	Provide ear protection as part of required PPE for average noise levels over above 85 dB.
BG11 Medium	Causes skin irritation and can cause serious eye irritation and/or damage. Harmful if swallowed. Can intensify fire.	Provide proper PPE (gloves, fire-resistant clothing, eye protection).
NaOH	Serious eye damage, can be corrosive to metals, causes skin corrosion.	Provide NIOSH-approved respiratory protection/breathing apparatus.

Environment

There is only one major waste stream of the plant (in each module), which occurs after a purge of the water/culture medium mixture after the ammonia has been removed by the membrane. The primary concern of the waste stream is its high pH (9.4) due to sodium hydroxide. Thus, it is recommended to mix with sulfuric acid or HCl to neutralize the solution, and then to send the stream to waste treatment. A recommended strategy for removal and recovery of sodium hydroxide from industrial wastewater includes a two-stage diffusion dialysis and electrodialysis process.[55] Further research on best practices for waste treatment of NaOH is recommended to ensure all best practices are met.

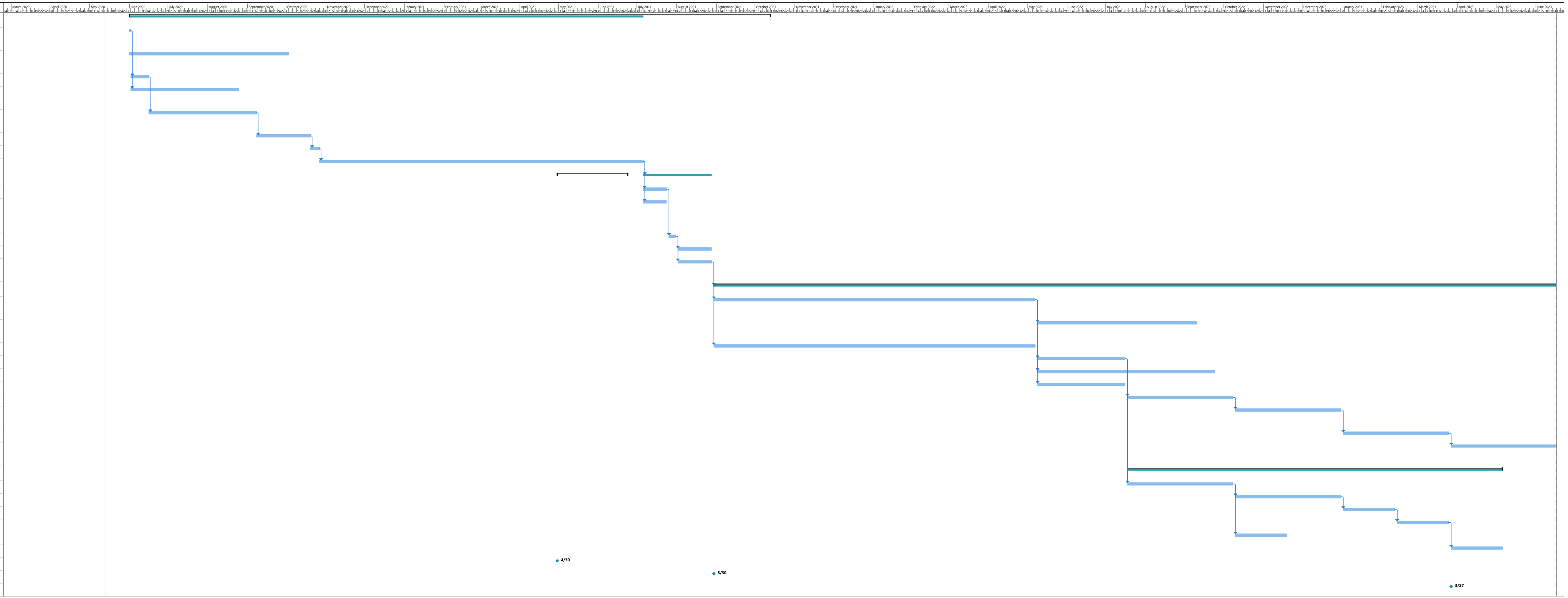
To summarize the action steps that should occur if this preliminary work gets approved, a scheduling chart was developed for the plant's construction. This includes a 6-month period for obtaining permit approvals relevant to environmental regulations. The major tasks include further detailed design and pilot-scale development focused on cyanobacteria production rates, supply chain analysis and purchasing, construction and safety, and start-up of the plant. The following table summarizes the schedule, which has a total time of 35.5 months, a conservative estimate for modular plants. The schedule reflects recommendations that both field construction and equipment purchasing not begin until permits are issued. The inspections are an imperative part of the schedule, as fabricated and installed equipment must meet all OSHA, ASME, and environmental regulations.

Main Items & Subtasks	Duration	Start Date	Predecessors
Detailed Design	**357 days**	**Mon 6/1/20**	
Decide if plant should proceed	1 day	Mon 6/1/20	
Conduct pilot-scale cyanobacteria research	90 days	Mon 6/1/20	
Develop plant-wide P&ID	10 days	Tue 6/2/20	2
Conduct detailed mechanical design	60 days	Tue 6/2/20	2
Conduct detailed electrical design of control systems	60 days	Tue 6/16/20	4
Conduct HAZOPs Review	30 days	Tue 9/8/20	6
Submit permit requests	5 days	Tue 10/20/20	7
Obtain permit approval	180 days	Tue 10/27/20	8
Supply Chain	39 days	Fri 4/30/21	9
Compile list of vendors	14 days	Tue 7/6/21	9
Obtain quotes on piping, instrumentation, and process equipment	14 days	Tue 7/6/21	9
Select Vendors	5 days	Mon 7/26/21	11
Order process equipment	20 days	Mon 8/2/21	13
Order instrumentation and piping	20 days	Mon 8/2/21	13
Construction and Safety	470 days	Mon 8/30/21	15
Complete foundational infrastructure	180 days	Mon 8/30/21	15
Construct greenhouse modules	90 days	Mon 5/9/22	17
Fabricate process equipment	180 days	Mon 8/30/21	15
Inspect fabricated equipment	50 days	Mon 5/9/22	19
Install wind turbines	100 days	Mon 5/9/22	17

Install battery storage	50 days	Mon 5/9/22	17
Install process equipment	60 days	Mon 7/18/22	20
Assemble piping & instrumentation	60 days	Mon 10/10/22	23
Complete I/O wiring	60 days	Mon 1/2/23	24
Calibrate installed equipment	60 days	Mon 3/27/23	25
Start-Up	210 days	Mon 7/18/22	
Train operators	60 days	Mon 7/18/22	20
Troubleshoot possible issues	60 days	Mon 10/10/22	28
Update SOPs	30 days	Mon 1/2/23	29
Update Spec Sheets	30 days	Mon 2/13/23	30
Conduct safety analysis	30 days	Mon 10/10/22	28
Begin operating plant	30 days	Mon 3/27/23	31
Milestones			
Permits Obtained		Fri 4/30/21	
Construction Begins		Mon 8/30/21	
Plant is Operational		Mon 3/27/23	
Total Time	**35.5**	**Months**	

The following page provides this plant construction schedule in a Gantt Chart format.

ID		Task Mode	Task Name	Duration	Start	Predecessors
1			**Detailed Design**	**357 days**	**Mon 6/1/20**	
2			Decide if plant should proceed	1 day	Mon 6/1/20	
3			Conduct pilot-scale cyanobacteria research	90 days	Mon 6/1/20	
4			Develop plant-wide P&ID	10 days	Tue 6/2/20	2
5			Conduct detailed mechanical design	60 days	Tue 6/2/20	2
6			Conduct detailed electrical design of control systems	60 days	Tue 6/16/20	4
7			Conduct HAZOPs Review	30 days	Tue 9/8/20	6
8			Submit permit requests	5 days	Tue 10/20/20	7
9			Obtain permit approval	180 days	Tue 10/27/20	8
10			**Supply Chain**	**39 days**	**Fri 4/30/21**	**9**
11			Compile list of vendors	14 days	Tue 7/6/21	9
12			Obtain quotes on piping, instrumentation, and process equipment	14 days	Tue 7/6/21	9
13			Select Vendors	5 days	Mon 7/26/21	11
14			Order process equipment	20 days	Mon 8/2/21	13
15			Order instrumentation and piping	20 days	Mon 8/2/21	13
16			**Construction and Safety**	**470 days**	**Mon 8/30/21**	**15**
17			Complete foundational infrastructure	180 days	Mon 8/30/21	15
18			Construct greenhouse modules	90 days	Mon 5/9/22	17
19			Fabricate process equipment	180 days	Mon 8/30/21	15
20			Inspect fabricated equipment	50 days	Mon 5/9/22	19
21			Install wind turbines	100 days	Mon 5/9/22	17
22			Install battery storage	50 days	Mon 5/9/22	17
23			Install process equipment	60 days	Mon 7/18/22	20
24			Assemble piping & instrumentation	60 days	Mon 10/10/22	23
25			Complete I/O wiring	60 days	Mon 1/2/23	24
26			Calibrate installed equipment	60 days	Mon 3/27/23	25
27			**Start-Up**	**210 days**	**Mon 7/18/22**	
28			Train operators	60 days	Mon 7/18/22	20
29			Troubleshoot possible issues	60 days	Mon 10/10/22	28
30			Update SOPs	30 days	Mon 1/2/23	29
31			Update Spec Sheets	30 days	Mon 2/13/23	30
32			Conduct safety analysis	30 days	Mon 10/10/22	28
33			Begin operating plant	30 days	Mon 3/27/23	31
34			**Permits Obtained**	0 days	Fri 4/30/21	
35			**Construction Begins**	0 days	Mon 8/30/21	
36			**Plant is Operational**	0 days	Mon 3/27/23	



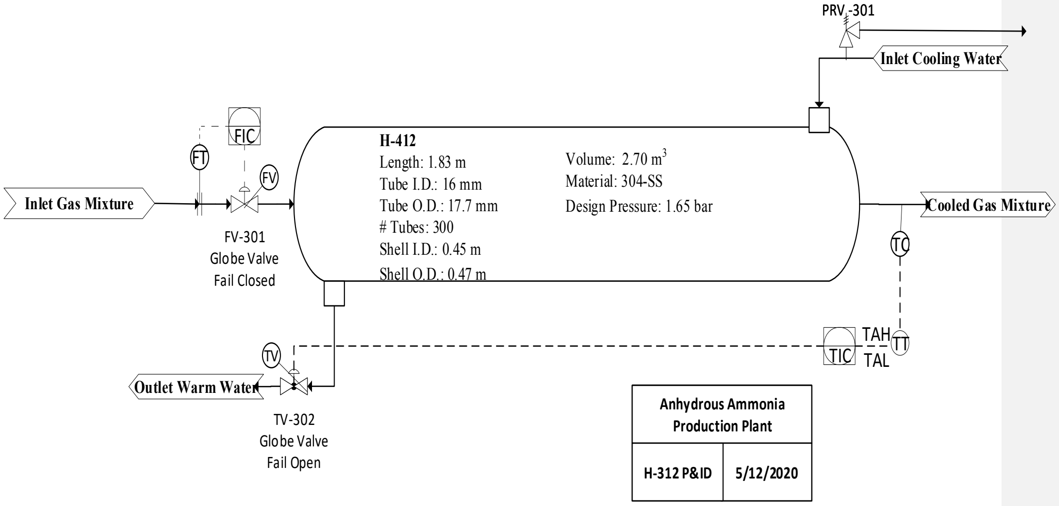
Project: Schock_AIChEGanttCha
Date: Wed 5/13/20

Task
Split
Milestone ◆
Summary
Project Summary
Inactive Task
Inactive Milestone ◇
Inactive Summary
Manual Task
Duration-only
Manual Summary Rollup
Manual Summary
Start-only [
Finish-only]
External Tasks
External Milestone ◆
Deadline ⬇
Progress
Manual Progress

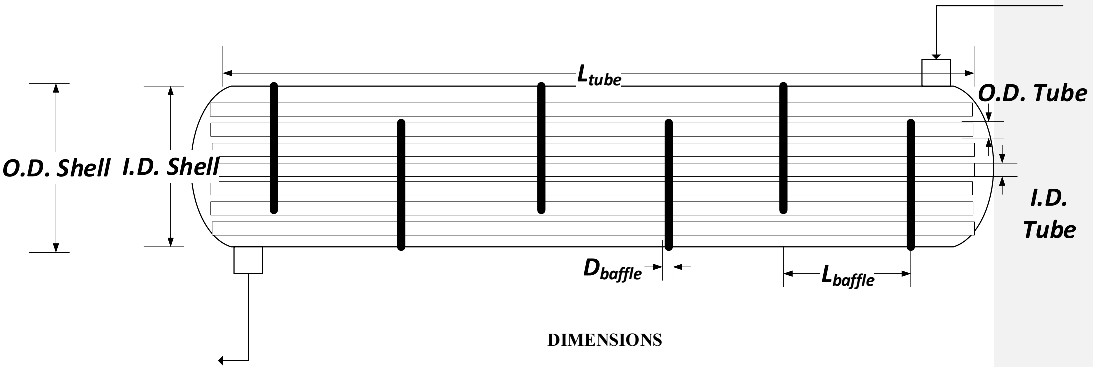
XV. Process Safety Considerations

P&ID

To emphasize consideration of detailed design and process safety control systems, a P&ID and dimensioned drawing was produced for H-312. Detailed calculations for tube sizing, number of tubes, shell diameter, number of baffles, and tube pitch spacing were based on the Tubular Exchanger Manufacturers Association (hereafter referred to as TEMA) and design procedures for shell & tube heat exchangers provided in Chapter 19 of Towler and Sinnott's *Chemical Engineering Design*, and were discussed in Section VI. For H-412, the P&ID and dimensioned drawing are provided below.



For this heat exchanger, the gas outlet temperature is measured by some temperature element, such as a thermocouple, which sends an electrical signal to a temperature transmitter. A temperature alarm high and temperature alarm low signal is present for safety. The transmitter sends the signal to a primary-mounted shared display temperature indicating controller. The temperature controller then sends an electrical signal to TV-302, a globe valve (fail open), which adjusts the cooling water flowrate. For safety, this valve was placed on the outlet of the cooling water to ensure there was flow going through the heat exchanger and that cooling water would be present in the heat exchanger in case of a blocked outlet. A pressure relief valve (PRV-301) was placed on the inlet of the cooling water, and provides emergency relief in case of rapid vaporization of the cooling water inside the heat exchanger. Finally, the gas mixture inlet flowrate is measured by an orifice and adjusted to try and maintain a constant gas flowrate, which helps to minimize required changes in the cooling water flowrate. A dimensioned drawing of this heat exchanger is shown below, describing the number of baffles, inner and outer diameters, length, and number of tubes.



DIMENSIONS

O.D. Shell	0.47 m	D_{baffle}	7.0 mm
I.D. Shell	0.45 m	L_{baffle}	0.26 m
I.D. Tube	16 mm	L_{Total}	1.83 m
O.D. Tube	17.7 mm	N_{Tubes}	300

OPERATING CONDITIONS

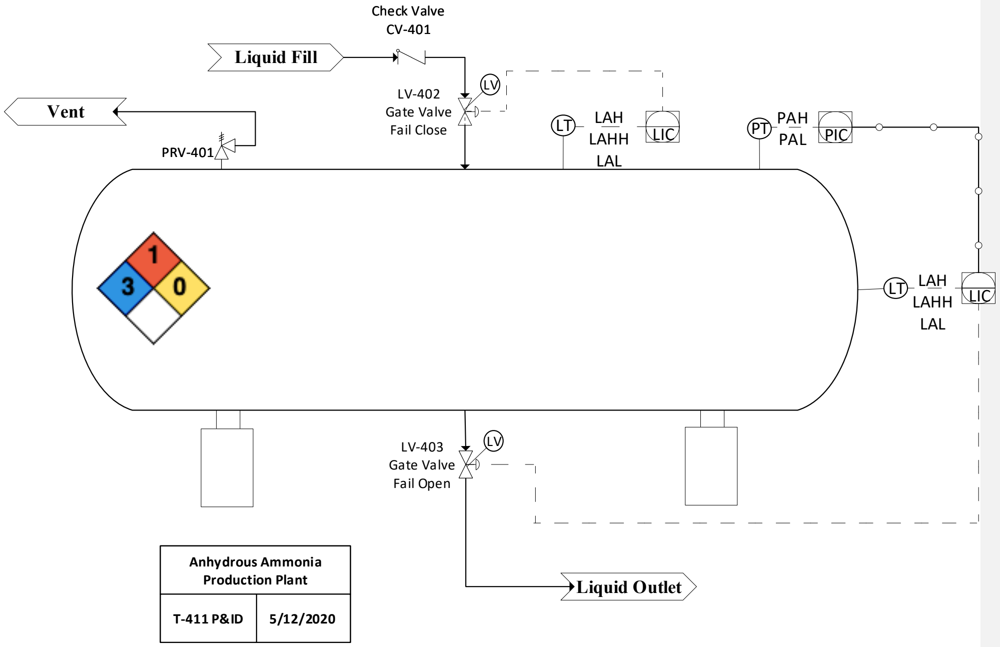
Ammonia/Air Mixture

Temperature	*377→200*	°C
Pressure	*1.5*	bar

Cooling Water

Temperature	*20→50*	°C
Pressure	*1.0*	bar

All heat exchangers in the purification section were designed as single-pass shell and tube heat exchangers, and the varying dimensions were summarized in the Specification Sheets. Due to the abundance of historical ammonia production incidents related to storage tanks, another P&ID was developed for the storage tanks for this plant. Key safety concerns were addressed by this P&ID.



Notable safety features of the storage tank include the cascade control for liquid removal and the presence of two level controllers. The cascade control allows for precise control over the level and pressure in the tank. Specifically, level control monitors for changes in liquid level, which could be caused by leaks, and the pressure controller can monitor vapor levels. The gate valve (LV-403) opens in case of rapid vaporization (where pressure relief needed), or when the level is too high. It would close if the liquid level is too low. It can also be manually controlled for operators to prepare the anhydrous ammonia product for transport. The level controller on top of the tank detects for high or low levels, and provides a secondary level measurement in case one controller fails. The check valve (CV-401) prevents reverse flow of any process vapors or liquids. The pressure relief valve (PRV-401) provides emergency pressure relief in case of rapid vaporization. Finally, the NFPA diamond for anhydrous ammonia should be present on all storage tanks to denote the hazards present in the system. Having clear signs indicating the hazards present around the plant is imperative to ensuring a safety culture exists and to manage risks.

To justify the types of valves used in the plant, the following table goes over each valve type, location, and reasoning for the purification and storage sections of the plant. Mixing valves (MV-303 through MV-311) were shown in the PFD for the purification section.

Valve #	**Type**	**Justification**
MV-303/ 304/305	3-Way Plug valve	On/off capabilities to send flows to different absorbers at different times of absorption cycle.
MV-306/ 307/308/309/ 310/311	3-Way Mixing Valve	Mix absorber/desorber effluents depending on cycle times.
PRV-301	Pressure Relief Valve	Emergency pressure relief of cooling water in case of rapid vaporization or blocked outlet.
FV-301	Globe Valve (Fail Close)	Maintains constant gas mixture inlet flow to HX based on orifice flow measurement. Fail close to stop gas flow in case of loss of heating.
TV-302	Globe Valve (Fail Open)	Varies cold water flow based on outlet gas temperature, out outlet of cold water to ensure cooling water remains in HX in case of blocked outlet.
PRV-401	Pressure Relief Valve	Emergency pressure relief of ammonia in case of vaporization (with proper ventilation)
CV-401	Check Valve	Prevent reverse flow of gases or liquids.
LV-402	Gate Valve (Fail Close)	On/off valve for liquid filling of ammonia tank, off if near overflow.
LV-403	Gate Valve (Fail Open)	On/off valve for hose to prepare ammonia for transport. ON if transport in use, or ON if level or pressure too high & draining necessary.

An example of three types of safety analyses (Checklists, What-ifs, and HAZOP) is provided for the heat exchanger H-312.

Checklist

ITEM	COMPLETED	DOES NOT APPLY	FURTHER STUDY REQUIRED
Material compatibility	**X**		
Corrosion	**X**		
Temperature control?	**X**		
Pressure relief adequate?			**X**
Safe Venting?			**X**
High/low level alarms	**X**		
Process Dynamics to Inform Control System?			**X**
Flash point?			**X**
Pressure Drop?			**X**

Overall Heat Transfer Coefficient?	**X**		
Blocked Outlet?	**X**		
Solids Build-up?			**X**

What If?

What If	**Consequence**
Cooling water leaks	Loss of product purity.
Blocked outlet	Pressure build-up in system.
Power failure	Control system fails, possible loss of cooling
Cooling flow decreases	Outlet gas temperature too high.
Process gas mixture flow increases	Outlet temperature could be too low, more cooling water utility required.
Cooling water rapidly vaporizes	Loss of cooling, possible explosion if pressure not relieved.

HAZOP

Intent: Cooling   Guide Word: No

Deviation	**Causes**	**Consequences**	**Safeguards**	**Actions**
No Cooling	Blocked outlet	Possible explosion Temperature increases Cooling water vaporizes.	Cooling water control valve on outlet Gas outlet temperature alarm	Add temperature alarm Schedule maintenance to check for blocks or solid buildup during shutdowns.
	Heat transfer area insufficient	Gas temperature increases over time	Cooling water flowrate increases through temperature control system	Conduct pilot-scale test of overall heat transfer coefficient

These safety analyses are not exhaustive, and if the plant were to proceed, a more detailed HAZOPs study is recommended for all sections of the plant. Process safety studies should be conducted with individuals from a variety of backgrounds and with varying expertise to ensure an inherently safe design can be implemented.

XVI. Other Important Considerations

Material Compatibility

Key design decisions were made for materials of construction in the plant. Specifically, material compatibility data was obtained for key chemicals in the plant. The table below summarizes this information, with an A rating meaning very good compatibility, a B rating meaning some compatibility issues could result depending on operating conditions, and an I rating meaning the material is incompatible with the chemical for various reasons. A color code was also implemented, with green corresponding to compatible, yellow corresponding to suitable under certain conditions, and brown denoting an incompatible material.

Material	**Ammonia (NH_3)**	**Water (H_2O)**	**Air (O_2/N_2)**	***$MgCl_2$/silica* (Absorbent)**
Aluminum	**A**	**A**	**A**	**I**
Carbon Graphite	**A**	**A**	**A**	**A**
Carbon steel	**B**	**I**	**A**	**B**
Cast Iron	**A**	**I**	**A**	**I**
Polypropylene	**A**	**A**	**A**	**A**
PVC	**A**	**A**	**A**	**B**
SS 304	**A**	**A**	**A**	**I**
SS 316	**A**	**A**	**A**	**I**
Brass	**I**	**A**	**A**	**I**
Bronze	**I**	**A**	**A**	**B**
Copper	**I**	**B**	**A**	**A**
Polycarbonate	**I**	**A**	**A**	**A**
Polyurethane	**I**	**A**	**A**	**A**

The materials of construction for each equipment part is provided in Section IX. Nearly all equipment was constructed with compatible "A" rating materials such as SS 304 or SS 316, however a notable decision was made in the material of construction for the absorbers/desorbers. Although carbon graphite was compatible with all primary chemicals in the plant, little information could be found on its use in industrial equipment. It was thus decided that carbon steel be used for the absorber because of the low water content in the streams entering and exiting the absorber/desorber (<0.5 wt%) and the reasonable compatibility agreement seen for ammonia, the absorbent, and air with carbon steel.

Land Requirements

The designed ammonia synthesis plant has a very large land requirement. The land required for the photobioreactor alone was 1121 acres. Additionally, the plant required over 30,000 wind turbines to supply all of the power that it needs to operate. Windmills generally require about 1.5 acres per turbine of this size, meaning that the turbines would require an additional 47,600 acres to set up. The total land footprint of the proposed chemical plant is nearly 50,000 acres of land. This amount of land for a single ammonia synthesis plant is incredibly high, especially compared to traditional plants with a similar production capacity.

The price of land has not been factored into the economic analysis, because it was already observed that the plant would not be profitable due to its large capital cost. In future, if plant changes can be made to reduce the capital cost of the plant, land cost will also need to be factored in to profitability calculations.

XVII. Conclusions and Recommendations

Although this novel approach to small-scale ammonia production can minimize the carbon footprint of the ammonia industry, preliminary research and design suggests it would not be profitable or realistic to achieve. With a net present value of –$347 billion, it is heavily recommended that this current plant design not be built. The largest source of operating cost for the plant was the capital related costs, which seems to indicate that the capital required to build this plant is largely what is keeping it from being profitable. That assessment also makes intuitive sense, since the currently designed plant would have a land footprint of over 1000 acres, and would be moving over 2.3 million cubic meters of fluid every day.

Improving the productivity of the cyanobacteria and finding a method to minimize the required flowrates in the plant would significantly decrease both capital and manufacturing costs. Because cyanobacteria have not been heavily studied for this application, it is expected that substantial gains can be made to increase the ability of these bacteria to produce ammonia. Currently, all research has these cyanobacteria in incredibly dilute solutions, and producing a small amount of ammonia. If the amount of ammonia produced by individual cyanobacteria can be increased, or the cyanobacteria's tolerance for increased cell density can be raised, or a combination of these two methods, large reductions in plant volume, energy requirement, and capital costs are all expected. The large energy requirements come from the pumps for the photobioreactors, which must pump a highly turbulent culture medium. Decreasing the flow velocity would likely decrease energy requirements by several orders of magnitude. A lower flowrate would also allow for more reasonable centrifuge sizes, and thus a more economically-optimal number of parallel modules could be employed. Some advantages to this plant include its low waste generation and high modularity, meaning production could be upsized or downsized with ease. The fact that the cyanobacteria actually uptake some carbon dioxide while synthesizing ammonia is also a benefit of this design. If this plant design becomes economical, its implementation could change the ammonia production process from emitting 1-3% of global carbon dioxide emissions to serving as a carbon sink, slowly rectifying the emissions from past fertilizer production processes.

It is recommended that the current design not be implemented due to unrealistic energy requirements and capital expenditures. Instead, research and development on using cyanobacteria for the purpose of ammonia production is recommended. If the cyanobacteria ammonia production rate is increased, it is possible the plant could be profitable. Furthermore, the novel membrane and selective absorption methods for removal and purification of ammonia appear to be effective for a small-scale anhydrous ammonia production plant. In particular, selective absorption has been used in academic studies to achieve up to 95% conversion of ammonia using reactive separation for the traditional Haber-Bosch process. Exploring alternative small-scale ammonia production methods, such as reactive separation and non-thermal plasma synthesis, would be valuable for comparison to the novel photobioreactor method and a decision on the optimal current technology to be used in a 50 mtpd plant. If the photobioreactor production rates are improved through further research and development, it is recommended that this design be reexamined. To conclude, further action on this current design is not recommended, and alternative methods for small-scale, greenhouse-gas independent ammonia production are recommended to be explored.

XVIII. Acknowledgements

We would like to thank all of the University Faculty involved in our Chemical Engineering education over the past four years. Combined, they have taught us the skills necessary to design this industrial plant, and have shown us how to apply both technical and soft skills in our future careers.

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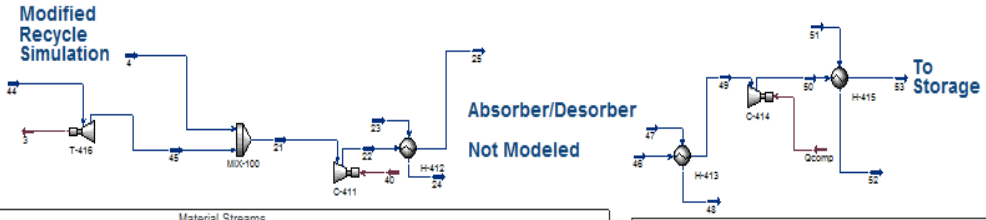
XX. Appendix

Aspen HYSYS Modeling

Aspen HYSYS was used to complete more complicated thermodynamic calculations for some processes in the plant. Specifically, it was used to model compression and heat exchanger calculations in the purification section of the plant. A NRTL-RK fluid model was used for all simulations. This was chosen because NRTL effectively models localized-composition non-ideal activities in liquid mixtures, and RK can model non-idealities for gaseous mixtures. The Redlich-Kwong equation of state is typically more accurate than the van der Waals equation at high temperatures such as those achieved during compression and absorption/desorption. Due to the complexities and transient nature of the absorption/desorption process, it could not be modeled in HYSYS, and instead had calculations based on literature and mass transfer principles. Hand calculations were used to obtain the initial flowrates, compositions, and operating conditions for the purification section.

The simulation was divided into two sections: before absorption and after desorption. Before absorption, there was a dependency on the recycle of the air exiting the absorber. The vacuum pump was estimated as a turbine with 75% efficiency. Hand calculations were used to determine starting compositions and flowrates after the membrane. Stream numbers align with those used in the PFD of the plant.



Material Streams									
		46	49	47	48	50	53	51	52
Vapour Fraction		1.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
Temperature	C	392.0	50.00	20.00	50.00	361.3	30.00	20.00	30.00
Pressure	kPa	100.0	100.0	100.0	90.00	1379	1379	100.0	90.00
Molar Flow	kgmole/h	122.3	122.3	759.0	759.0	122.3	122.3	5425	5425
Mass Flow	kg/h	2084	2084	1.367e+004	1.367e+004	2084	2084	9.773e+004	9.773e+004
Liquid Volume Flow	m3/h	3.377	3.377	13.70	13.70	3.377	3.377	97.92	97.92
Heat Flow	kJ/h	-3.845e+006	-5.578e+006	-2.165e+008	-2.148e+008	-4.041e+006	-8.163e+006	-1.548e+009	-1.543e+009
		44	45	4	21	22	25	23	24
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000
Temperature	C	200.0	39.21	80.00	40.06	377.3	200.0	20.00	50.00
Pressure	kPa	150.0	17.33	17.33	17.33	150.0	150.0	101.0	91.00
Molar Flow	kgmole/h	7089	7089	122.6	7212	7212	7212	1.737e+004	1.737e+004
Mass Flow	kg/h	2.042e+005	2.042e+005	2107	2.063e+005	2.063e+005	2.063e+005	3.129e+005	3.129e+005
Liquid Volume Flow	m3/h	236.0	236.0	3.191	239.2	239.2	239.2	313.5	313.5
Heat Flow	kJ/h	3.039e+007	-3.513e+006	-9.374e+006	-1.289e+007	6.121e+007	2.157e+007	-4.954e+009	-4.915e+009

Compositions								
	46	49	47	48	50	53	51	52
Comp Mole Frac (Ammonia)	0.9962	0.9962	0.0000	0.0000	0.9962	0.9962	0.0000	0.0000
Comp Mole Frac (H2O)	0.0038	0.0038	1.0000	1.0000	0.0038	0.0038	1.0000	1.0000
Comp Mole Frac (Nitrogen)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (Oxygen)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	44	45	4	21	22	25	23	24
Comp Mole Frac (Ammonia)	0.0001	0.0001	0.8330	0.0142	0.0142	0.0142	0.0000	0.0000
Comp Mole Frac (H2O)	0.0037	0.0037	0.1670	0.0065	0.0065	0.0065	1.0000	1.0000
Comp Mole Frac (Nitrogen)	0.7870	0.7870	0.0000	0.7736	0.7736	0.7736	0.0000	0.0000
Comp Mole Frac (Oxygen)	0.2092	0.2092	0.0000	0.2056	0.2056	0.2056	0.0000	0.0000

Energy Streams				
		Qcomp	3	40
Heat Flow	kJ/h	1.537e+006	3.390e+007	7.409e+007

Photobioreactor Design Considerations

Cyanobacteria

In order to choose a strain of cyanobacteria, there were several deciding factors. The most important was the cyanobacteria needed to secrete the ammonia/ammonium into the culture medium for it to be able to be collected. The process by which cyanobacteria produce ammonia from nitrogen is called nitrogen fixation, and typically that ammonia is then converted into glutamine via the glutamine-synthetase pathway so that the nitrogen is in a more useful form for the cell. For the cyanobacteria to excrete ammonia into the medium, this reaction needs to be altered or blocked. Many of the studies looking at ammonia production by cyanobacterium use a chemical called L-methionine-D,L-sulphoximine (MSX) in order to block this secondary reaction.[48,] However, the glutamine synthetase reaction is important to cell survival, and although these experiments had higher detection of ammonia (when compared to no MSX in medium), the cells were unable to live very long because the blocked reaction created a deficiency in nitrogenous compounds.[48,] The chemical MSX is also very expensive, and since it would have to be replaced it ended up being a huge operating cost. Another much cheaper glutamine synthetase inhibitor, a fungicide called Bastivin (popular to India), was also considered, but it would have to be continually added to the culture and then there would still be the problem of the cells not being able to function well. Overall, because of the cost and the complications with cell function it was decided that these inhibitors were not a good approach to solving this problem.

Instead of inhibiting the glutamine-synthetase reaction, there is another process that could be altered to increase ammonia/ammonium output. The nitrogen fixation reaction that creates ammonia and ammonium is facilitated by an enzyme called nitrogenase that is actually inhibited by the presence of ammonium.[49] Consequently ammonia/ammonium will not buildup in the cell if it is not being used in the glutamine-synthetase reaction as quickly as it is made. Scientists have been able to derepress nitrogen synthase in the presence of ammonium, so that ammonia/ammonium is continually made in many strains of cyanobacteria.[49,46] The most compelling studies looked at altered strains of *Anabaena variabilis* and *Anabaena siamensis*.[46,49] Since these altered strains are difficult to find for sale (most can only be obtained by contacting the university/researchers that created them and asking for a sample), it is likely that for this chemical plant a unique strain would have to be developed. In order to get a rough estimate on what culture requirements and outputs would look like, a study by Thomas, Zaritsky, and Boussiba that included detailed culture procedures and cyanobacteria properties and produced a strain of cyanobacteria, *A. siamensis*, which had average ammonia production outputs when compared to similar studies was chosen as a basis for the calculations for this plant.[46]

Photobioreactor Structure

There are several different structures that were considered in creation of the photobioreactor (PBR) system including: flat plate PBRs, horizontal tubular PBRs, vertical tubular PBRs, triangular PBRs, plastic bag PBRs, and immobilized medium PBRs. Raceway ponds were not considered for cultivation of cyanobacteria because the concern with culture contamination. Vertical tubular PBRs were determined to be the best design because a smaller area is required, photosynthetic efficiencies were highest, and they allowed for an easy flow-through design.[52]

Systems using immobilized mediums were heavily considered because cyanobacteria produced higher amounts of ammonia while immobilized when compared to free-floating.[46,53,54] However, because a continuous system was needed there were some design complications with using the cyanobacteria in immobilized beads. A packed bed reactor using the cyanobacteria in immobilized beads was considered as well as immobilizing the cyanobacteria in sheets and having solution flowed across them, but because ammonia production is cell density dependent and cells would have to be removed and replaced throughout production, it was decided that it was not feasible to use immobilized mediums and a tubular vertical PBR with free-floating cyanobacteria in medium was chosen.

In designing the vertical PBR, height and diameter drastically change the amount of area and flow rate required. Typically, vertical tubular PBRs have small diameter pipes because of light requirements of cyanobacteria and the penetration depth of light through the PVC and water. Smaller diameters allow for more light to be hitting each of the cells which in turn promote higher biomass production. However, smaller diameters ultimately end up costing more and taking up more space than larger diameters. Because of these tradeoffs, it was decided that 6 inch diameter would be sufficient for this process, since this is toward the higher end of pipe diameters used for PBRs and our concentration of cyanobacteria is small so there is less concern with the cyanobacteria blocking each other from accessing sunlight.

Because cyanobacteria create ammonia in very dilute amounts and there is a high production requirement (50mtpd), the volume of the plant and flow rates in the PBR are very high. Typically in tubular photobioreactors, the flow rate throughout the PBR is set by the gas flow rate. However, for this plant that would require a incredible amount of gas and the volume produced by it would increase the required volume drastically. So instead of that, a gas flow rate was set as 0.05 vvm by aeration recommendations for culture in a PBR.[58]

Since Minnesota on average only has on average 190 sunny and partly cloudy days, light supplementation is required for the plant to operate 365 days per year. Fluorescent light tubing was placed between every other row of the PBR in order to supplement light in the most efficient way.[59]

pH

Typically, *Anabaena* strains are cultured in medium with a pH of ~7.[46,49,50] However, in water ammonia is in equilibrium with ammonium based on the pH.[47] Since our membranes work best to remove ammonia from the solution, we need the pH of our culture medium to be above 9.3 (the pH equilibrium threshold into the ammonia-dominating regime).[47] Since a strain of cyanobacteria will likely have to be developed for use in the plant, it is recommended to take this into consideration and selectively choose cyanobacteria that can function well at higher pH's. It has been observed that internal processes in *A. variabilis* like O_2 evolution are only severely inhibited at pH >9.5, so creation of a alkaline strain is plausible.[51] Because of this study and the ammonia-ammonium equilibrium curve, the preliminary design of this plant includes a pH of 9.4. Raising the pH of the culture medium will be done by adding small amounts of sodium hydroxide.

Costing Calculations

CAPITAL COST ESTIMATING:

M-210:

The molar flow rate through the membrane is known. Firstly, unit conversions are needed to get the molar flow rate in terms of a mass flow rate.

$$m_{NH_3,33} = \frac{2.15\ kgmol}{hr} * 17.03 \frac{kg}{kgmol} = 36.6 \frac{kg}{hr}$$

With the mass flow rate of the ammonia through the membrane known, the ammonia flux from the CSIRO study can be used to determine a required membrane area per module.

$$A_{M-210} = \frac{m_{NH_3,out}}{J_{NH_3}} = \frac{36.6*10^3 \frac{g}{hr}}{16 \frac{g}{m^2*hr}} = 2287.5\ m^2$$

With the surface area of the membrane per module determined, the cost of the membrane unit per module can also be determined. Another source stated that for largescale ordering of membranes for water treatment applications, membranes cost less than \$16/m^2. This was the only data that could be effectively found for costing membranes, so a pricing of \$16/m^2 was used to cost this apparatus. It is expected to be a rough estimation but is also expected to get a decent ballpark estimate for the price of the membrane module. The removal of ammonia from wastewater is commonly done, so a wastewater treatment membrane seems to be very similar to the application used here.

$$C_{M-211} = \frac{\$16}{m^2} * 2287.5\ m^2 = \$36{,}600$$

HX-211:

To cost the heat exchanger, first the surface area for heat transfer needs to be determined. The first piece of required information is the log mean temperature difference for the heat exchanger. This is calculated below.

$$\Delta T_{lm} = \frac{\Delta T_2 - \Delta T_1}{ln \frac{\Delta T_2}{\Delta T_1}}$$

$$\Delta T_{lm} = \frac{(242-80)℃-(242-42)℃}{ln \frac{(242-80)℃}{(242-20)℃}} = 180.3\ ℃$$

An overall heat transfer coefficient of 2000 W/m^2-K was assumed as well, which is an intermediate value for expected heat transfer coefficients between steam and aqueous solutions (Welty). With an overall heat transfer coefficient assumed, the surface area for heat transfer can be calculated using the heat exchanger design equation.

$$A_{H-211} = \frac{q_{H-211}}{U*\Delta T_{lm}}$$

$$A_{H-211} = \frac{73.0*10^6\ J}{2000 \frac{W}{m^2-K} * 180.3\ ℃} = 202.5\ m^2$$

With the surface area of the heat exchanger determined, there are many correlations available to cost the unit. The online Peter and Timmerhaus calculator was used to cost this heat exchanger. A shell and tube heat exchanger rated for 5000 kPa made of 316 stainless steel was used to estimate the price of this unit. This yielded a capital cost of \$38,386. It is worth noting that this pricing was for the year 2003, meaning that a correction factor using plant indices is required.

$$C_{H-211,present} = \frac{C_{e,present}}{C_{e,2003}} * C_{H-211,2003}$$

$$C_{H-211,present} = \frac{599.5}{390.4} * \$38{,}386 = \$58{,}900$$

The heat exchanger H-211 has an estimated capital cost of $58,900 for the first module.

HX-212:

To cost the heat exchanger, first the surface area for heat transfer needs to be determined. The first piece of required information is the log mean temperature difference for the heat exchanger. This is calculated below.

$$\Delta T_{lm} = \frac{\Delta T_2 - \Delta T_1}{ln \frac{\Delta T_2}{\Delta T_1}}$$

$$\Delta T_{lm} = \frac{(80-40)\text{°C} - (42-30)\text{°C}}{ln \frac{(80-10)\text{°C}}{(42-5)\text{°C}}} = 23.26\ \text{°C}$$

An overall heat transfer coefficient of 750 W/m^2-K was assumed as well, which is an intermediate value for expected heat transfer coefficients between water and aqueous solutions (Welty). With an overall heat transfer coefficient assumed, the surface area for heat transfer can be calculated using the heat exchanger design equation.

$$A_{H-211} = \frac{q_{H-211}}{U * \Delta T_{lm}}$$

$$A_{H-212} = \frac{73.0*10^6\ J}{750 \frac{W}{m^2-K} * 23.26\ \text{°C}} = 4185\ m^2$$

With the surface area of the heat exchanger determined, there are many correlations available to cost the unit. The online Peter and Timmerhaus calculator was used to cost this heat exchanger. A flat plate heat exchanger made of carbon steel was used to estimate the price of this unit. The highest the correlation went up to was an area of 1500 m^2, which yielded a capital cost of $118,193. So this value was used as a scaling factor, and served as a ration for the price of the heat exchanger, resulting in a final purchase price of $329,800. It was assumed that these costs scaled by the maximum area would serve as a reasonable estimation for the price of a larger heat exchanger. It is worth noting that this pricing was for the year 2003, meaning that a correction factor using plant indices is required.

$$C_{H-212,present} = \frac{C_{e,present}}{C_{e,2003}} * C_{H-212,2003}$$

$$C_{H-212,present} = \frac{599.5}{390.4} * \$329{,}800 = \$506{,}400$$

The heat exchanger H-212 has an estimated capital cost of $292,000 for the first module.

B-211:

To price the heating element required to vaporize the high-pressure water, a correlation from Towler and Sinnot was used. The Towler and Sinnot correlation requires the mass flow rate of steam through the heater to calculate, in kg/hr.

$$m_{28} = 41.66 \frac{kg}{s} * \frac{3600\ s}{hr} = 150000 \frac{kg}{hr}$$

With the steam mass flow rate determined, the price of heater can be determined. S is the mass flow rate of steam calculated above, while a, b, and n are tabulated values. For a field erected boiler, able to withstand between 10 and 70 bar, a is 130,000, b is 53, and n is 0.9.

$$C_{B-211,2010} = a + b * S^n$$

$$C_{B-211,2010} = 130000 + 53 * (150000)^{0.9} = \$2,427,000$$

Again, this cost for the boiler must be converted to present day dollars. This will be done using the chemical plant indices for the present and for 2010, when Towler and Sinnot was published.

$$C_{B-211,present} = \frac{599.5}{532.9} * \$2,427,000 = \$2,730,000$$

T-210:

The mixing tank was assumed to give the fluid a 1 hour residence time, to allow sufficient time for reintroduction of the cyanobacteria into the cell medium before sending it back through the plant. This allowed for the calculation of the volume of the storage tank.

$$V_{T-210} = \tau * v_{23} = 1\,hr * \frac{2383488\,m^3}{day} * \frac{1}{60\,modules} * \frac{1 day}{24\,hr} = 1655.2\,m^3$$

The online Peter and Timmerhaus calculator also has the ability to calculate tank prices based on tank volumes. This tool was used, assuming a volume of 1660 m^3 and a tank built out of 316 stainless steel, to determine a purchase price of \$334,163. Again, since this is for the year 2003, a correction using chemical plant indices is required to get a capital cost for the current year.

$$C_{T-210,present} = \frac{C_{e,present}}{C_{e,2003}} * C_{T-210,2003}$$

$$C_{T-210,present} = \frac{599.5}{390.4} * \$334,163 = \$513,100$$

C-211 and C-212:

Pricing data for centrifuges range from \$1,000 to \$50,000, depending on size. It was assumed that centrifuges would cost about \$10,000 each.