Ammonia Synthesis for Fertilizer Production

A Major Qualifying Project Report

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MQP Report

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Contents:

Abstract:

This reviews the history of the ammonia industry and its use as a nitrogen rich fertilizer. Current ammonia industries were analyzed economically and environmentally, and the specifications from current ammonia plants were compared with the patented process illustrated in Chapter 3 of the paper. The economic comparison shows a breakeven point for a current medium-scale ammonia plant to be five years with a production cost of \$600/ton, where the patented process plant can break even in less than two years and has a relative production cost of \$232/ton. It was found in the environmental comparison that the patented process, if scaled globally, would address and eliminate 7% of the total CO_2 emissions on the planet. Lab works as well as calculations were made to predict and recommend continuing research to further optimize the industrial production of ammonia and related fertilizers.

Chapter 1:

Introduction and Background

Introduction:

In solid or liquid states, ammonia salts and solutions are the active components of most synthetic fertilizers used in agriculture, which consume 83% of the world's ammonia and warrant higher demands for ammonia production.[1] The primary industrial method for ammonia synthesis is the Haber-Bosch process, created by Fritz Haber in 1905 and developed for industry by Carl Bosch in 1910. The overall process synthesizes ammonia from molecular nitrogen and hydrogen by feeding the reactants over iron catalysts at a high pressure and temperature, requiring bulky, well-insulated reactors to house the process. The Haber process synthesizes approximately 150 million tons of ammonia each year and has allowed the earth to sustain a population nearly five times larger than before the procedure's invention. However, the use of natural gas as a source of hydrogen and energy needed to derive nitrogen from atmospheric air have been the subjects of environmental concern.[2] The industrial use and geological extraction of natural gas are known to contribute to carbon dioxide emissions and water pollution, respectively, and today an estimated 59% of natural gas produced in the United States is used in ammonia synthesis to meet the high demand of gaseous hydrogen.[3] Approximately 80% of ammonia synthesized today is eventually converted into urea fertilizer, a dense nitrate that is more stable at room temperature, allowing easier storage and transportation than ammonia.

To truly understand the significance of ammonia and urea as fertilizers, one should understand the impact of treating soil with an effective fertilizer. Plants generally require soil containing high amounts of available nitrogen, phosphorus and potassium, as well as other minor nutrients.[4] Synthetic and organic fertilizers can be used to successfully obtain this nutrient balance and optimize plant growth, though synthetic fertilizers tend to work more consistently than organic fertilizers, which are typically made from plant and animal wastes and tend to vary in composition. Thus, the global demand for synthetic nitrogenous fertilizers has reached new heights, with the 2012 global market generating over $98.6 billion and estimated to reach $114 billion by 2018.[5] Considering that, in 2012, the industrial production of ammonia in the United States alone was responsible for 9.4 million tons of carbon dioxide emissions, it is obvious that the worldwide production of ammonia and urea must be monitored and reformed to handle the expected increase in usage.[6] However, in order to make necessary changes to these industries, different options for ammonia and urea synthesis, as well as any potential environmental and economic effects that may result from these options, should be assessed.

Background:

Due to their usage in the manufacturing of gunpowder and explosives, European chemists in the late 1700s developed an interest in obtaining and synthesizing diverse nitrogenous compounds such as nitric acid, sodium nitrate and ammonia, beginning research into the synthesis of these compounds that would last for over a century. In the 1840s, German chemist Justus von Liebig discovered nitrogen to be one of several nutrients essential to plant growth, leading to the widespread use of nitrogenous compounds in fertilizers.[7] Nitrogen was originally taken from natural deposits in the earth, such as the Atacama Desert of Peru and Chile (rich in "Chilean saltpeter" that could be converted to nitric acid). However, in the 1870s, ammonia was first created industrially as a byproduct in the production of coke, though this method of ammonia synthesis could yield only two-thirds of the nitrogen exported from South America.[8]

In the late 1800s, chemists agreed that the demand for nitrogenous compounds would likely soon exceed the natural supply, catalyzing the search for more effective industrial processes.[9] The creation of the Haber process in 1905, and its subsequent industrial scale-up by Carl Bosch in 1910, marked the first practical procedure for synthesizing anhydrous liquid ammonia from hydrogen and atmospheric nitrogen. This process is still used industrially today. This procedure has proven sufficient for meeting synthetic ammonia demands and the abundance of both reactants suggests that the Haber process may be the most sustainable option possible, though increased demands and a scarcity of resources may encourage the development of alternative methods.

To increase the rate of ammonia synthesis to produce the necessary amount of product, the temperature must be raised to the range of 400 - 500°C, with pressure increased to 15 – 25 MPa to compensate for the high temperature. The Haber process also relies on heated iron catalysts to break the bonds of molecular nitrogen, and requires frequent cooling phases to maintain a manageable equilibrium constant and repeated recycling of unreacted hydrogen and nitrogen to achieve a higher overall conversion (approximately 18% of reactants are converted to ammonia in each pass).[10] These conditions can only be met with the protection of expensive reaction vessels, that are strengthened and insulated to withstand the necessary pressures and temperatures, and the high consumption of electricity, and in many cases, the reaction byproduct carbon dioxide is released into the atmosphere where it is detrimental as a greenhouse gas.

Fritz Haber and Carl Bosch, the developers of the Haber-Bosch process were each awarded Nobel prizes for their work, on the basis that they had overcame many difficulties associated with reliable fertilizer manufacturing and high-pressure technology at an industrial scale. The significance of their contribution became clear as agriculture improved across the world, allowing the global population to increase from 1.6 billion people in 1900 to over 7 billion alive today.[11] However, many suspect that, if population increases at the same rate as it has over the past century, the carrying capacity of earth will be tested and earth's population could expand to the point where food demand exceeds supply, ensuring death for many who will starve due to insufficient food. Even today, the global population relies greatly on a consistent supply of food being produced, and any large instability in crop yields is capable of leaving a noticeable percentage of the population without food.[12] Due to the dependence of crop prices on fertilizer prices, it can be assumed that the first people to lose access to food will be those who can no longer afford to feed themselves.

Modern agricultural yields are similar from season to season due to the consistent performance of synthetic fertilizers and their unchanging composition, making nitrogenous fertilizers a more reliable choice than organic fertilizers which vary in nutrient content. About 50% of nitrogen applied to crops is absorbed while the remainder is lost to the soil and because this nitrogen is easily manufactured, fertilizer is abundantly reapplied to assure that the minimum required nitrogen will be available to all plants. However, nitrogenous compounds such as ammonia and nitric acid can pollute soil and groundwater when used in excess, and the runoff is potentially harmful to plants and animals depending on the nitrogen concentration. Humans, particularly small children, have been known to suffer health complications from living in areas with heavy use of synthetic fertilizer due to the excess nitrogen in the area's soil and water, or from eating fish that were contaminated.[13]

The environmental consequences of fertilizer manufacturing consist not only of ground pollution, but include emissions into the atmosphere. The agricultural industry is responsible for 10% of total greenhouse gas emissions worldwide, according to the EPA, not including the release of carbon dioxide as a byproduct or any pollutants emitted due to ammonia synthesis.

Chapter 2:

Current Ammonia Industry

Today, the processes by which ammonia and urea are synthesized can be summarized as simplified stoichiometric equations:

Ammonia $N_2 + 3H_2 \rightarrow 2NH_3$

Then in another plant:

Urea $2NH_3 + CO_2 \rightleftharpoons (NH_2)_2CO + H_2O$

While this project focuses on the production of ammonia, 80% of the ammonia manufactured today becomes feedstock for the manufacture of urea, a more stable nitrate used for fertilizer. However, the modern syntheses of ammonia and urea require several necessary and costly processes and treatments to achieve the highest yield possible, which must be considered to accurately assess their effectiveness, as well as their impacts on the environment and industry.[14]

Ammonia Synthesis:

The leading method for the industrial production of ammonia has been the Haber-Bosch process for nearly a century worldwide. The overall process requires high temperatures and pressures and utilizes nitrogen fixation (reacting atmospheric nitrogen), continuous flow and the frequent recovery of unreacted gases, resulting in a method capable of producing large amounts of ammonia more efficiently than earlier methods of synthesis. Development of the process was accompanied by advancements in large-scale, continuous-flow, high-pressure technology and today, approximately 159 million tons of ammonia are produced annually through similar or slightly-modified industrial processes.[15]

Stoichiometrically, the reaction of one mole of nitrogen with three moles of hydrogen produces two moles of ammonia in an exothermic process. The reaction, however, is unfavorable on its own and is made possible through the manipulation of physical factors. To lower the activation energy required for synthesis, the reactants (both in gas phase) are passed over an iron catalyst with an added potassium hydroxide promoter for increased efficiency. The reaction is reversible in nature, though the production of ammonia can be made favorable using Le Chatelier’s Principle, which dictates that an increase in pressure makes the reaction favor the side with fewer moles, ammonia in this case. However, the pressures required to optimize ammonia synthesis are very high and expensive to use industrially at a large scale, so a compromised pressure of typically 200 atm is often used. While Le Chatelier’s Principle also suggests that low temperatures would cause the reaction to favor ammonia production, low temperatures slow the reaction to impractical rates, leading manufacturers to apply a compromised temperature of 400-450°C. Each time the reactants undergo this process, only 10-18% of the potential ammonia is converted, but by recycling unreacted gas, no reactants are wasted or lost and, after muliple passes, 97% of the reactants can be converted overall. While nitrogen is reacted from air (reducing the amount of feedstock to be purchased or transported and stored), hydrogen gas must be produced, most often through the catalytic steam reforming of natural gas: the process by which steam is reacted with natural gas (methane) at high temperatures from 700-1100°C to produce bulk hydrogen and carbon monoxide. Approximately 98% of ammonia is currently produced with natural gas as feedstock using steam shifting, though a minority obtain hydrogen from coal or through the catalytic reforming of naptha. Interestingly, as hydrogen is mixed with air at the start of the reaction, many molecules of atmospheric oxygen react with hydrogen to form water, removing the oxygen gas which comprises 21% of air.[14]

Having been in practical use for over a century, the Haber-Bosch process has undergone countless modifications and adaptations. Not only would the industrial equipment used in the 1910s be considered outdated today, advancements in technology have allowed manufacturers to experiment with altering the process or equipment to optimize production. As a result, not all ammonia plants worldwide use an identical process or facility, though the general process has remained largely consistent. Among plants that use catalytic steam reforming, six general steps are taken to produce synthetic ammonia: Natural gas desulferization, catalytic steam reforming, carbon monoxide shift, carbon dioxide removal, methanation and ammonia synthesis. A process flow diagram of a typical ammonia plant can be seen in Figure 2.1.[15]

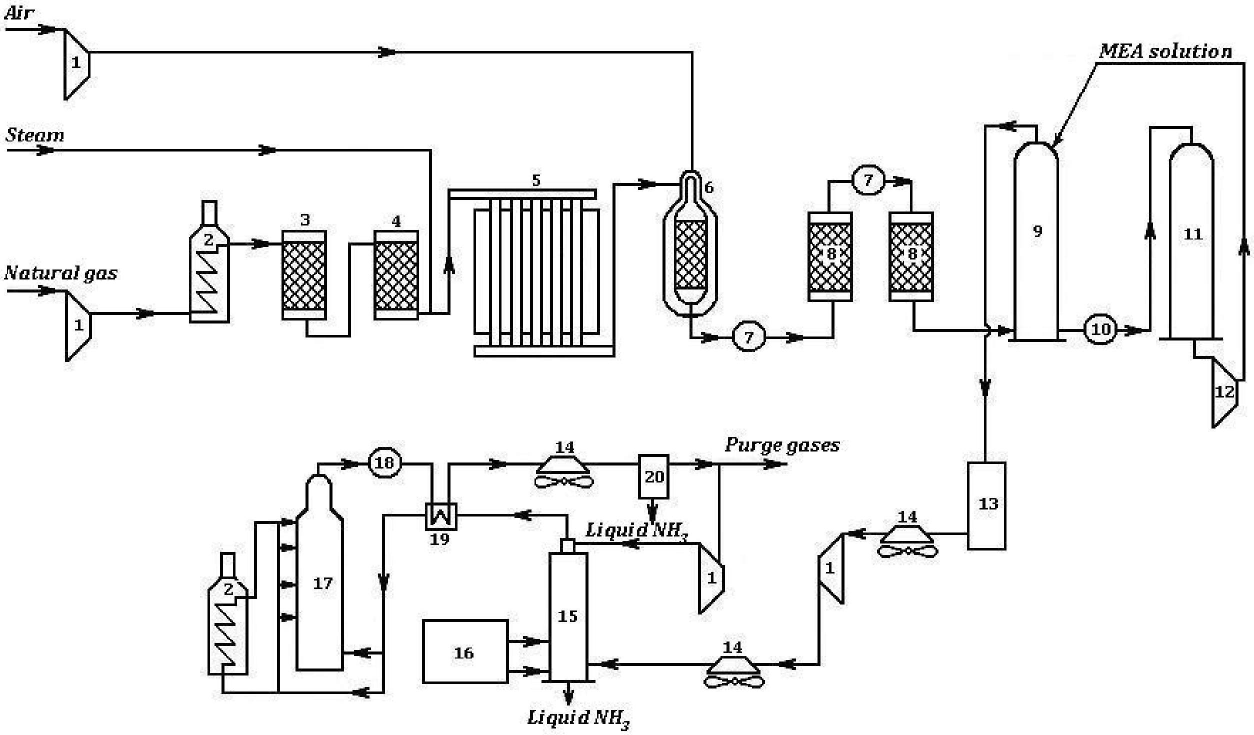


Figure 2.1: Ammonia Production Process Flow Diagram[16]

The Haber-Bosch process has remained the most common industrial method of ammonia manufacturing since its development, and though the most common commercial fertilizers contain ammonium sulfate, ammonium phosphate and urea as ingredients, these chemicals are all converted industrially from ammonia. Of the 150 million tonnes of ammonia synthesized each year, approximately 83% goes to the manufacture of fertilizers needed for agriculture.[2] Given the high demand of ammonia and the high production capacity of plants that synthesize it, one might assume that the Haber-Bosch process and, by extension, the ammonia and fertilizer industries, occupy a niche market in all nations, and are not likely to change due to a lack of feasible alternatives. However, practices within these industries have been called into question by environmentalists, many of whom believe the current process of ammonia production leads to greenhouse gas emissions and the release of toxic chemicals.

Economics of Ammonia:

Similar to any industrial process, ammonia manufacturing has undergone decades of development to optimize production and reduce prices wherever possible. Many large-scale plants across the world are built near natural gas reserves to reduce the cost of transporting feedstock, but because of the centralization of plants in many countries, ammonia must be transported to all corners of the country to satisfy agricultural needs. Currently, ammonia can be sold from a factory at an average cost of $750/ton, but due to the process' reliance on natural gas, fluctuations in natural gas prices could significantly increase production costs for ammonia manufacturing. Therefore, the cost of ammonia is susceptible to rapid change in the event of a scarcity of natural gas, which is a fossil fuel of which an assumedly finite amount is available. Subsequent fluctuations in ammonia price may have significant consequences at larger scales, such as large farms limited by the increased cost of fertilizer.[17]

Faced with higher feedstock costs, ammonia plants are given the option to reduce production or cut costs in other facets of production where affordable alternatives are available. Recent decades have shown minor adjustments made to the current industrial method of ammonia synthesis without drastic changes to the overall process, though some plants continue to apply experimental techniques to substitute for a more commonly-used process within the broader process of ammonia production, for the purpose of reducing either costs or pollution. A modern ammonia plant is expected to continue production for up to 15 years of operation, reaching a break-even point after about five years.[18] The largest costs involved in ammonia production are operating costs which include the recurring cost of natural gas, accounting for 75% of a plant's operating costs. This and other aspects of the process are eligible for replacement, leaving a variety of options available for lowering costs. Experimentation into alternative affordable feedstock has been common in the past and will likely remain a consistent pursuit throughout the development of all major ammonia synthesis processes.

Environmental Impact of Ammonia Sythesis:

The majority of greenhouse gases emitted as a result of ammonia synthesis are released through the preparation of hydrogen from the feedstock. A dramatic example would be the ammonia manufacturing plants in China, 80% of which use coal as feedstock as oppoosed to natural gas or naptha. Hydrogen is produced from coal through gasification (or partial oxidation), in which the coal is reacted with oxygen and steam at high temperatures and pressures. The reaction produces a synthesis gas containing hydrogen and carbon monoxide, the latter of which is reacted with excess hydrogen to form carbon dioxide which can then be removed. While plants that use coal as feedstock make up the minority of plants worldwide, China currently produces more ammonia than any other country in the world. Of the 70 million tons of ammonia produced in China annually, an estimated 80% was synthesized with hydrogen from coal - this accounts for a sizable fraction of the world's total ammonia production.[19]

For most plants worldwide, natural gas is much more affordable than coal or heavy oil as a feedstock, and natural gas is considered to be the most sustainable of these fuels. However, the use of a cleaner feedstock does not render manufacturers unable to release the same potentially harmful compounds. In processes using the catalytic steam forming of natural gas (the vast majority of existing plants), carbon monoxide formed from the catalytic steam reforming step is reacted with excess hydrogen to form carbon monoxide, which is more easily removed from the system, similar to the process used for coal gasification. Through scrubbing, any residual carbon dioxide can be heated and purged from the system, occasionally through vents releasing it into the atmosphere. Plants have designed methods of capturing the carbon dioxide produced through steam forming, preventing the gas from entering the atmosphere and potentially repurposing the compound by feeding it into another process in which carbon dioxide is a reactant. Considering the majority of ammonia is converted to urea before it is used in fertilizers, it seems practical for carbon dioxide to be captured from steam forming and used as a reactant in urea synthesis. However, many smaller ammonia plants and plants that operate independently of urea production simply vent these fumes to the atmosphere, and even plants that recycle carbon dioxide emissions in the synthesis process where the gas is not as easily captured. The Intergovernmental Panel on Climate Change (IPCC) notes that the only plants that do not release carbon dioxide during the synthesis process are those that use a pure hydrogen feedstock rather than natural gas, which makes up a very marginal percentage of plants.

Though carbon dioxide emissions are a primary concern, several other compounds produced in ammonia synthesis are considered harmful pollutants if released into the environment. Vented regeneration steam from regeneration of the desulfarized bed contains sulfer oxides and hydrogen sulfide, both of which are hazardous air and water pollutants. The same step can potentially emit carbon monoxide as well as many combustion products (i.e. nitrogen oxides, hydrocarbons, particulates) that reduce air quality in high concentrations. Throughout nearly all ammonia synthesis processes, scrubbers and strippers are used in an attempt to isolate and remove any hazardous compounds before they can be emitted. However, the emission of pollutants is evident in this industry, and if such preventative measures are ineffective then process modification should be considered.[15]

Chapter 3:

Patented Ammonia Process

The invention and development of the Haber-Bosch process had a remarkably unique impact on the shaping of modern science and human history. Due to worldwide industrial use of the Haber-Bosch process throughout the 20th Century, crops were grown and produced at quantities large enough to sustain growing populations, resulting directly in an exponential rise in the earth's population. However, this impressive contribution should not absolve the process of its shortcomings: As the human race continues to grow rapidly in population and potentially test the earth's carrying capacity, it becomes increasingly necessary to evaluate current and proposed agricultural processes.

Though the Haber-Bosch process has been used and adapted to produce extensive quantities of nitrogenous fertilizers and satisfy agricultural demands for the past several decades, the threat of further population growth and harmful chemical emissions has inspired engineers to seek and design alternative methods for fertilizer production with the goal of increased or more steady agricultural yields One novel process, which was filed for a provisional patent, has been optimized by its patent-holder to be employed within this project and evaluated as a potential ammonia production alternative for the near future. Designed for use in Saudi Arabia, the process aims to utilize and repurpose the byproducts from other industrial processes. This patented process synthesizes ammonia from exhaust gas leaving a carbon black refinery, using liquid water and atmospheric air as sources for molecular hydrogen and nitrogen, respectively.

Carbon black possesses a range of unique properties that have made it desirable for a variety of applications. Today, the carbon compound is used most commonly as a reinforcing agent in plastic and rubber products, as pigment in paints and inks, and occasionally as automobile and aerospace coating, due to the improved conductivity and UV protection provided by the compound. In the United States, 90% of carbon black is manufactures through the oil furnace process in which a liquid hydrocarbon is heated, continuously pumped into the combustion zone of a natural gas furnace and quickly cooled, ultimately producing carbon black through the incomplete combustion of the feedstock hydrocarbon.[20] The exhaust gas from this process contains mostly CO with variable concentrations of sulfides SO_2 and H_2S, and is fed into a scrubber where the exhaust contaminants are mixed with water and dissolved CO is separated from the mix. A water-gas shift reaction can then be undergone with the addition of excess water, converting carbon monoxide and water to carbon dioxide and molecular hydrogen, the latter of which provides a suitable feedstock for ammonia synthesis.

There is no reason to doubt that the CO feedstock needed to match the current worldwide production of ammonia synthesis would be fully satisfied by the emissions from carbon black manufacturing and the manufacture of related products. Currently, the production of plastics reinforced with carbon black yields over 18 billion pounds of plastic, forming 1,400 pounds of CO for each pound of plastic.[20] Assuming the earliest full-scale ammonia manufacturing plants using this patented process could be built and in operation by the year 2020, the amount of CO formed from carbon black plastic production already provides enough feedstock to satisfy the year's ammonia production projected of 250 million tons, assuming exhaust CO is effectively captured and saved and/or immediately processed. Considering the requirements of the water-gas shift reaction and the worldwide availability of water, this ammonia synthesis process will be available for use and adaptation wherever carbon black production is sufficient, potentially raising the maximum amount of ammonia that can be produced yearly while widening the range of areas where ammonia synthesis can be performed industrially.

Process Description:

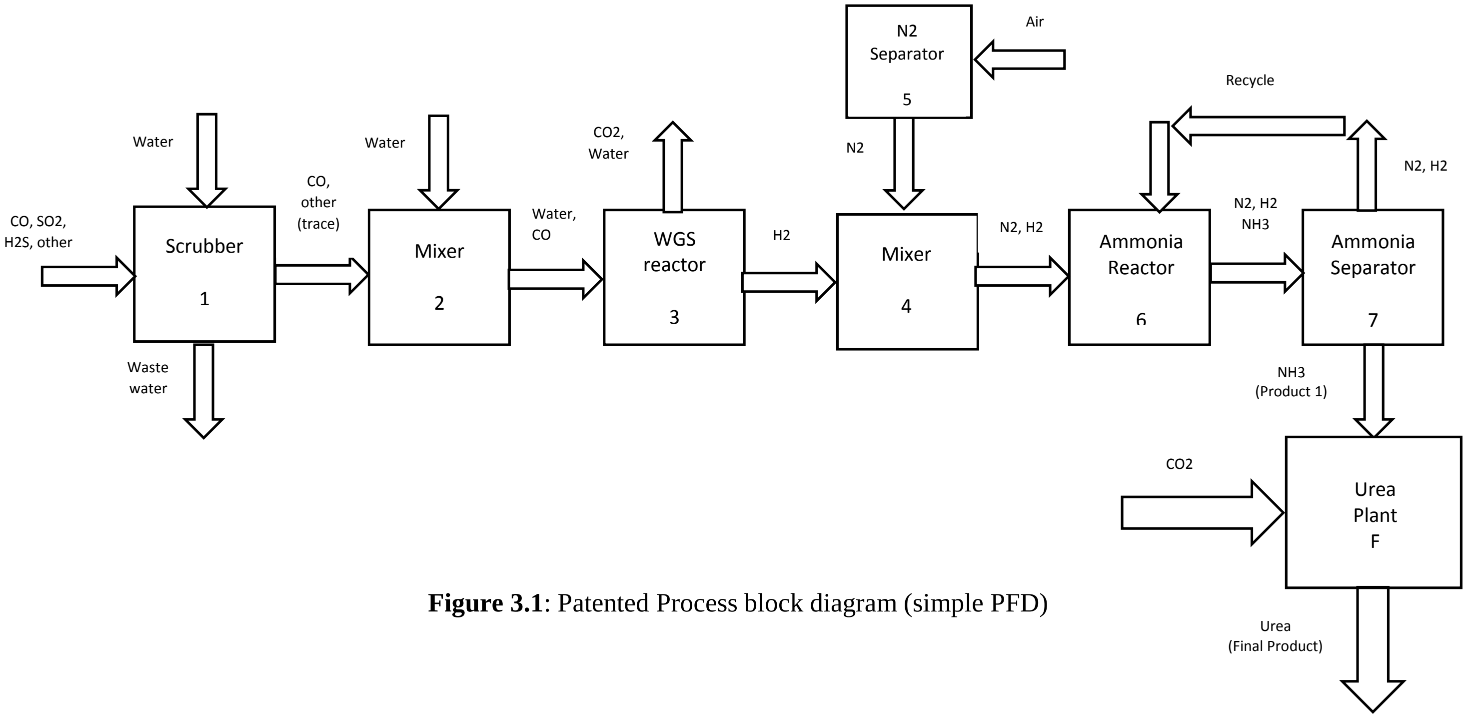


Figure 3.1: Patented Process block diagram (simple PFD)

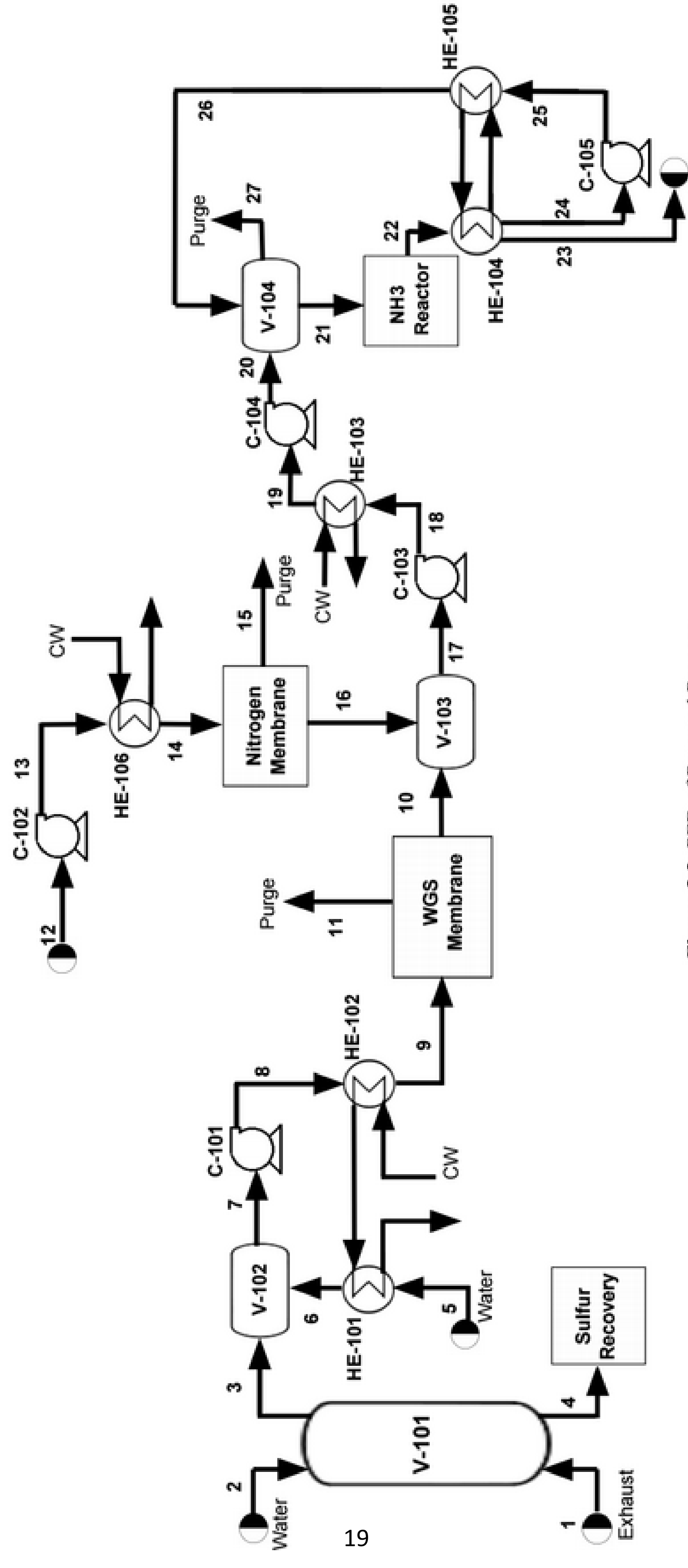


Figure 3.2: PFD of Patented Process

Table 3.1: Stream Data for PFD in Figure 3.2

Stream Number	**Stream Description**	**Contents**	**Temp (°C)**	**Pressure (psi)**	**Mass Flow Rate (kg/hr)**
1	Gas feed to Scrubber	CO, SO_2, HS_2, other	25	20	116,600
2	Water feed to Scrubber	H_2O	25	20	958,000
3	CO exit from Scrubber	CO	25	17	105,105
4	Sulfur Recovery input	H_2O, SO_2, H_2S, other	25	17	966,495
5	Water feed to Heater	H_2O	25	20	139,000
6	Heated water feed to Mixer 1	H_2O	127	17	139,000
7	Mixer exit	CO, H_2O	110	15	247,100
8	Pre-WGS Compressor exit	CO, H_2O	700	780	247,100
9	Pre-WGS Cooler exit	CO, H_2O	400	777	247,100
10	Hydrogen produced from WGS	H_2	400	20	7,355
11	WGS Purge	CO, H_2O	400	730	239,745
12	Air input to N_2 Compressor	Air	25	14.7	275,500
13	Air input to Air Cooler	Air	380	240	275,500
14	Air input to N_2 Membrane	Air	50	237	275,500
15	Air exit from N_2 Membrane	Air	50	235	223,960
16	Nitrogen feed to Mixer 2	N_2	50	20	51,485
17	Feed to 1st stage Compressor	H_2, N_2	170	18	58,840
18	Feed to intermediate Cooler	H_2, N_2	650	295	58,840
19	Feed to 2nd stage Compressor	H_2, N_2	185	290	58,840
20	Feed to Mixer 3	H_2, N_2	600	2955	58,840
21	Feed to Ammonia Reactor	H_2, N_2	450	2950	294,200
22	Ammonia Reactor outlet	H_2, N_2, NH_3	480	2650	294,200
23	Ammonia Product	NH_3	100	2645	58,800
24	Recycle kettle gas outlet	H_2, N_2	100	2645	235,360
25	Recycle Compressor outlet	H_2, N_2	115	2960	235,360
26	Recycle Heater outlet	H_2, N_2	415	2955	235,360
27	Purge		450	2640	40

As indicated in Figure 3.2 and Table 3.1 above, the plant design uses a total of five compressors, six heat exchangers, four vessels, one water-gas shift membrane, one nitrogen membrane, and one ammonia reactor, all of which fall under the category of capital costs. The equations preceding the design of each piece of equipment can be found in Appendix A. Initially, exhaust gas from a carbon black refinery or manufacturing plant enters a scrubber at a temperature and pressure of 25°C and 1 ATM where the gas components are mixed with water and the useful CO is separated from contaminants SO_2 and H_2S. Exiting the scrubber, the waste water stream of sulfides in water can be saved and used for sulfur recovery while product stream containing CO is mixed with fresh water at a 2:1 molar ratio of water to CO, then heated to 450°C in preparation for the water-gas shift reaction. This sulfur recovery is performed using lime, precipitating the contaminant sulfur. Lime is a very inexpensive compound, and the resulting solid can be repurposed as a filler in cement production plants.

For the WGS reaction, the heated stream of water and CO enters an Iron-Chromium catalyzed membrane reactor. With the help of palladium plating to improve and promote proton transfer, the reaction is undergone and pure hydrogen is separated and recovered while water and CO_2 in a 1:1 molar ratio comprise the waste stream. With the H_2 feedstock secured, a nitrogen membrane separator is used to isolate high-purity molecular N_2 from the air. H_2 gas is mixed with N_2 at a 3:1 molar ratio, heated and pressurized to 450°C and 200 bar, respectively, preparing the stream for the ammonia synthesis reaction. The reaction is similar to that of the Haber-Bosch process: A reactor, operating at a high temperature and pressure and equipped with an Iron-Chromium catalyst, reacts H_2 and N_2 and achieves a single-pass yield of approximately 18%, though the product ammonia is isolated using a membrane separator and the unreacted gases are fed back into the reactor until a total yield of approximately 98% of the reactant gases have been reacted.[10]

In the final steps of the designed process, the ammonia (still at a high temperature and pressure) is mixed with excess CO_2 produced in the carbon black refinery and reacted at a temperature and pressure of about 180°C and 150 bar, respectively. This stream is intended to be reacted into urea, a common nitrate, though the manufacture of urea is not detailed in the scope of this project. However, if the stream of NH_3 and CO_2 was used as the feedstock to a nearby urea synthesis plant, this would eliminate or alleviate the need to heat and pressurize the stream before synthesis, and the CO_2 formed as a byproduct in the WGS reaction could be saved and fed into the process, both improving urea yield efficacy and preventing the emission of a greenhouse gas.

Economics:

It is assumed that any capital costs associated with the plant's construction must be paid only once, as most equipment is expected to remain functional for fifteen to twenty years before being replaced and updated, though accidents or hardware problems may make it necessary to replace select pieces of equipment earlier to allow production to continue efficiently. In addition to the price of equipment, capital costs include the cost of land (if the land is purchased), the cost of labor to construct the plant, and any fees and taxes associated with construction and operation. Operating costs such as the costs of water, electricity usage and labor are separate from capital costs and calculated based on the plant's production rate because the cost of water or electricity reflects usage of these resources which depends on how much ammonia is manufactured.[21] [22]

Capital Cost

In order to estimate the cost of all equipment, the common engineering software Capcost was used (a screenshot of which is shown with other cost-deciding tools Appendix B). Using the design of a theoretical plant, the volumetric, temperature and pressure requirements were calculated for each piece of equipment and each unit was then selected through Capcost based on these specifications, as well as the material of construction. The software searches its own index of equipment and outputs the predicted price of each individual piece of equipment and the total price of all equipment added.

Of the five compressors needed to carry out this patented process, C-101 had an estimated price of $65.7 million, C-102 and C-103 were both estimated at $28.1 million, C-104 at $22.8 million and C-105 at $500,000, adding up to $145.2 million. For heat exchangers, HE-101 and HE-105, both heaters, are valued at $1.5 million and $2.2 million, respectively. HE-102, HE-103 and HE-106 are all coolers, valued at $2.5 million, $1.5 million and $3.8 million, respectively. HE-104, a kettle heater, is valued at $30.5 million, bringing the total estimated price of heat exchangers to $42 million. The first vessel (V-101) is a scrubber with an estimated cost of $670,000. The remaining vessels are all mixers, with V-102 and V-104 valued at $670,000 each and V-103 valued at $422,000, resulting in a total price of $2.43 million for all vessels. Capcost was also used to estimate the price of the ammonia reactor needed for this process, and using the estimation that the cost of catalyst reflects 10% of the reactor price, the reactor and embedded iron-catalyst were valued at $650,000.

The prices of the water-gas shift and nitrogen membranes were unattainable using Capcost. To predict the price of the desired nitrogen membrane, a vendor specializing in membrane separators was contacted, and the necessary membrane was given an estimated price of $15 million. For the WGS membrane, faculty of the WPI Chemical Engineering department were consulted, 200 Palladium plated membranes were needed at a price of $20 million was estimated including the cost of the membrane and catalyst. All equipment prices estimated using Capcost depend on the current Chemical Engineering Plant Cost Index (CEPCI). The prices generated by Capcost for this plant were estimated using a CEPCI value of 500, whereas the most recent annual average was calculated at 576.1, meaning the total cost of equipment predicted using Capcost had to be multiplied by a ratio of 1.15 to predict a more accurate value. Given that the sum of all equipment prices from Capcost is equal to $190.3 million, the CEPCI-adjusted price is valued at $219 million. Adding the predicted membrane prices, the full cost of equipment for the plant is estimated at $255 million.

Table 3.2: Percent added to Equipment Cost

Expense	**Percent added to Equipment Cost (%)**
Installation	50
Controls	20
Piping	30
Electricity	20
Extras	15
Insulation	10
Engineering	10
Legal Fees	10
Contingency	10
Total	175

As seen in Table 3.2, it was estimated that 175% of the calculated equipment cost was to be added to the equipment cost, resulting in a multiplier of 2.75 that, when applied to the equipment cost, provides the fixed capital cost. The fixed capital cost calculated for this process was $702 million. To determine these individual percentages, Monte Carlo simulations were run to gather results and indicate the minimum and maximum percentages that should be considered when calculating fixed capital cost. These published minimum and maximum percentages for each applicable cost were considered, and a likely percentage within range was chosen based on expected costs, as shown in Appendix A.1. From this analysis, it was estimated that the fixed instillation costs (which include foundation, construction materials and labor) should account for 50% more than previously predicted. The cost of controls, including sensors, wires and installation, are estimated at an additional 20%, as well as electricity, which includes the cost of circuit breakers, wiring and installation. Piping costs, accounting for the cost of pipes, pipe racks and valves, are expected to increase 30%, and extras, including minor costs such as valve fittings, are expected to increase 15%. A 10% cost increase was anticipated for the insulation of piping and heat-sensitive units, the cost of engineering labor and consultation, legal fees regarding permits and patents, and contingency as a buffer in the event of unforeseen circumstances.

Operating Cost

Apart from the cost of equipment and other initial purchases, the operating costs for this process depend on the amount of utilities consumed and the rate at which they are consumed, thereby reflecting the amount of ammonia produced by a plant. Considering this process was designed for ammonia production in Saudi Arabia, the costs of individual utilities were calculated based on the nation’s standard costs for industrial use.

When operated at full scale, this patented process is designed to consume 1517 tons of water per hour, fed into the system through streams 1 and 5 in Figure 3.2, and additional cooling water must be purchased by the plant to serve as an energy conduit in heat exchangers, though the cost is kept lower by recycling cooling water between two pairs of heat exchangers: HE-101 sharing water with HE-102 and HE-104 with HE-105. At a standard utility cost of $0.10/ton and assuming constant production (24 hours per day for 365 days), the annual cost of water for this process is estimated at \$1.5 million/year.[23] Production varies from one month to another based on ammonia demand, which fluctuates based on the product's agricultural application – however, for consistency, these utility costs were calculated or estimated using the assumption that overall production is steady and constant throughout a given year. At a cost of \$0.032/kwh, the plant's electricity usage is estimated at \$74.5 million/year, accounting for the plant's largest utility.[24] In Saudi Arabia, a plant can rent the land on which it operates from the government at a cost of \$0.25/m^2, making the cost of land an operating cost that must be paid yearly.[23] The designed plant requires an estimated 250,000 m^2 of land which can be rented for \$62,500 annually. Other utility costs must be considered, such as the cost of lime for sulfur recovery and the cost of waste disposal. A wide array of utilities are necessary for the plant to operate fully, but their individual costs are much smaller than that of water or electricity. For these miscellaneous operating costs, \$1 million/year should be allotted.

Operating costs are not limited to tangible or consumable utilities. Employees must be paid to operate and maintain the plant, and the number of employees must satisfy the plant's labor requirements. For this process to operate at full scale, a team of three engineers and five technicians working year-round should suffice, and paying a yearly salary of \$100,000 to all engineers and \$50,000 to all technicians costs the plant \$550,000/year for labor.[25] Besides the cost of labor for these employees, additional technicians and engineers must be hired occasionally to service or repair equipment, typically costing the plant 10% of its fixed capital cost every three to five years, as necessary. In order to better account for these expenses, the operating cost for servicing equipment can be recalculated to obtain an annual expense, costing the plant 4% of its fixed capital costs per year. With an equipment cost of \$255 million, servicing should cost the plant \$10 million/year. A plant must also pay royalties yearly for the right to use and profit from a patented process, costing the plant 3% in revenue from its yearly total production. This plant is designed to produce 515,000 tons/year of anhydrous ammonia, and assuming the product can be sold at \$750/ton, sales will generate a total of \$386 million per year, resulting royalty fees of \$11.5 million per year.[17]

Table 3.3: Operating Costs for Patented Process

Item	**Cost $M/year**
Water	1.5
Electricity	60
Maintenance	10
Random	1
Land	0.1
Labor	0.6
Royalties	11.5
Total	**84.7**

The price per ton of ammonia has risen steadily over the past several years, increasing at an average rate of 3% per year.[19] However, for these calculations, it was assumed that ammonia will continue to be sold at $750/ton for the next quarter century, compensating for inflation that would also lead to slightly increased capital costs. To calculate the return on investment (ROI), the expected profit made by the plant during its lifetime was divided by the plant's capital costs and operational costs, adjusted for each year the plant is estimated to continue production. Given an expected plant life of twenty years, ammonia sales will yield $7.72 billion (accumulating $386.25 million yearly) while operating costs will account for $1.69 billion ($84.7 million per year), with a fixed capital cost of $702 million. The profit made in this time would account for a current value of $5.33 billion which, divided by the combined capital and operating costs ($2.39 billion), gives a ROI of 223%, essentially earning the plant $2.23 for every dollar invested in its construction and operation. The cost of production of ammonia using this process is about $232/ton.

While production sales and operating costs remain linear throughout the life of the plant, expensive capital costs prevent the plant from achieving a significant profit during its first few years of operation. The break-even point, at which the plant's revenue from production exactly affords its capital and operating costs, signals the time at which the plant will begin accumulating profit, having paid off the initial capital costs. It was calculated that, after approximately 2.3 years of production, the plant will reach a break-even point, after which the plant will continue to profit from production for as long as it operates.

Environmental Considerations:

Many major considerations have been made regarding the plant's emissions and disposal of waste, in an effort to reduce the pollution released worldwide as a result of ammonia production. With the need for natural gas feedstock eliminated, the patented process encounters much less CO and CO_2 than the current process for ammonia synthesis, using only stored CO imported from a carbon black manufacturer. This CO is fed into the WGS membrane where it is consumed entirely, limiting the chances that this plant will emit CO into the atmosphere. The plant's sulfur recovery system also aims to remove sulfides SO_2 and H_2S and prevent their emission, and by donating the waste lime for cement manufacturing, the plant secures a safe disposal method for sulfides that also recycles sizable amounts of waste.

This process differs significantly from the current process in that much less CO_2 will be generated as a byproduct. The catalytic steam reforming of natural gas currently used to obtain H_2 feedstock contributes to over half of a plant's CO_2 emissions, and in 2009 alone, the use of natural gas feedstock in the United States was responsible for the release of 7.6 million tons of CO_2.[25] The substitution of a water-gas shift membrane over steam reforming suggests that any greenhouse gases produced or emitted by a current plant due to the use of natural gas feedstock will not be produced using this patented method. While typical plants emit CO_2 produced from the use of natural gas for heat exchangers (in addition to H_2 feedstock), the designed plant takes advantage of recycled water between heat exchangers, eliminating much of the need for external heating. Not only is the plant expected to yield substantial amounts of ammonia yearly with significantly reduced CO_2 emissions, the process makes use of greenhouse gas wastes recycled from carbon black plants and refineries while exporting its own CO_2 waste to be recycled in the production of urea (where all ammonia produced in this plant is expected to be used). The capture and reuse of greenhouse gases between plants and processes reduces the need for new feedstock to be collected or produced, while nearly eliminating the possibility that these waste gases will be emitted into the atmosphere where they could cause harm.

As with any, this patented process' true environmental and economic impact will come to light as the process is implemented and operated, and may prove less efficient and financially sustainable in reality than calculated. However, the process' design suggest that its global implementation would drastically reduce the emission of greenhouse gases compared to the current process. Emissions will still be produced by automobiles in the export of recycled wastes between plants – however, most current ammonia plants are located in close proximity to natural gas wells, and with water feedstock more widely available worldwide and less centralized than natural gas reserves, plants will be less limited geographically, making the local production of carbon black, ammonia and urea economically feasible. The manufacture of nitrogen fertilizers, including ammonia, urea and their derivatives, account for approximately 7% of the 9.9 billion tons of CO_2 emitted globally per year.[27] This supports the assumption that, if this process were to be developed for global use and successfully avoid the emission of CO and CO_2 as designed, the switch in ammonia manufacturing processes could potentially allow a 7% drop in global greenhouse gas emissions.

Chapter 4:

Future of Ammonia synthesis

In Chapter 3 of this report, the designed process relied on the coupling of ammonia and urea synthesis reactions to recycle and prevent the emission of greenhouse gases, making it practical to design the two processes with this collaboration in mind. In an effort to explore the potential benefits of coupling reactions in an ammonia synthesis process, this chapter addresses the possibility of running two reactions within close proximity: A reactor is placed in a pipe and designed to allow a WGS reaction to take place around the reactor, which contains an ammonia synthesis reaction driven by the hydrogen feedstock produced from the WGS. The broad purpose of these experiments is to generate reaction data that can be compared to a current process, demonstrating the potential benefits or shortcomings associated with coupling reactions. Evidence suggesting that this setup conserves reactor space, requires less energy or requires less human involvement can be helpful in the design of future processes as resources such as area and labor are exhausted. This chapter outlines innovative approaches or alternatives to the current industrial synthesis of ammonia, assessing options that have not yet been used for major production. These processes, if further developed, can prove to be practical alternatives for ammonia synthesis and, because the future availability of water, electricity and land worldwide is yet unclear, such innovative processes may prove to be necessary for large-scale synthesis in the coming century.

Coupling of Water-Gas Shift & NH_3 Reactions:

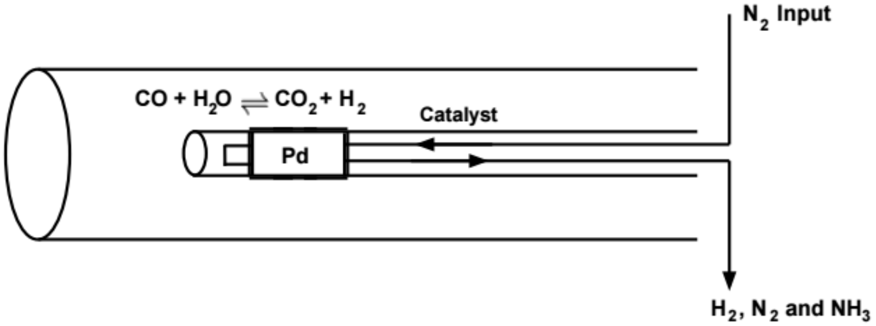


FIGURE 4.1: Diagram of Dual Reaction Approach

This proposed process, mentioned in the above paragraph and outlined in Figure 4.1 and Figure 4.2, is intended to take place within a pipe that houses a smaller reactor. In the process, a water-gas shift reaction is catalyzed on the outside of the reactor, providing heat and hydrogen feedstock for the ammonia synthesis reaction housed within the reactor. These reactions are summarized by the following simplified stoichiometric equations:

Water-Gas Shift:	$CO + H_2O \rightleftharpoons CO_2 + H_2$
Ammonia Synthesis:	$N_2 + 3H_2 \rightleftharpoons 2NH_3$

This combined process, if operated for commercial ammonia production, would make use of an iron catalyst for the WGS reaction and ammonia synthesis reaction, as well as palladium for increased proton transfer. However, this project is limited by a WPI project budget (allotting a two-member project group a total budget of $1,000) and, as a result, the use of palladium was omitted from the corresponding reactions. This omission was suggested by a lab advisor due to palladium's susceptibility to cracking from temperature change – to replicate the procedure and measure production at varying temperatures, a new bed of Pd would be needed for each reaction, making experimentation economically infeasible. However, given the volume of published data detailing the effect of Pd on production yield, a small-scale reaction was chosen for experimentation, with results focusing primarily on the ammonia yield under WGS conditions.

An analysis of the data produced from this reaction at variable temperatures would serve as the basis for many calculations and prediction's regarding the process' feasibility as a commercial industrial process, including the potential rate at which ammonia can be produced, and the associated residence time. From these data, one can analyze the efficiency and practicality of the process and estimate whether a large-scale adaptation of this process is commercially feasible, also considering factors such as a plant's land requirements and the availability of needed utilities. Even if the process is not concluded to be feasible or appropriate for modern use, the findings of this experiment can be recorded and the process can be recreated in the future to explore further applications or adapted for industrial use if necessary.

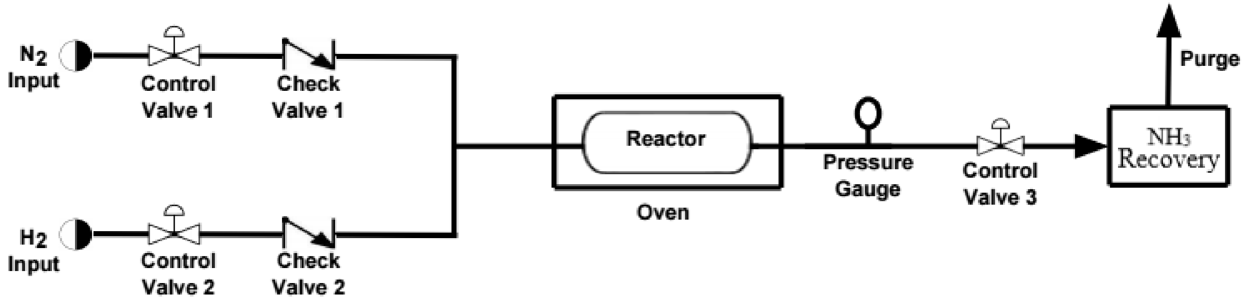


Figure 4.2: Simplified P&ID Design

Before the process could was designed or tested, the advisor of this project was contacted to discuss the concept of coupling reactions within ammonia production, resulting in the design of a process that could reasonably be operated and tested in the available lab space, outlined in Figure 4.2 as well as Appendix C. From the simple design, the lab manager for WPI's Chemical Engineering department helped to compile a full list of needed materials and equipment, shown in Appendix D. All materials from the list were reviewed and ordered by the department's administrative assistants and, upon the arrival of these materials, the reactor was built and all pipes and valves were secured in WPI's machine shop with the aid of the project advisor. The fully constructed reactor was moved to the lab station, lab safety precautions were reviewed, the reactor was placed in an oven within the lab area, two tanks of hydrogen and nitrogen were secured to their respective feed lines, the reactor's product stream was aligned to exit into an ammonia recovery vessel and the gaseous waste stream was vented to the lab hood, demonstrated in the photographs shown in Appendix E. The reactor was flushed multiple times with N_2 gas to test for leaks or blockages and also to purge any substance that could contaminate the sample. It was decided the reaction would be operated both as a steady-state and batch process, measuring the results of the steady-state reaction after 24 hours at three different temperatures and the batch results after one hour, also at three temperatures. Besides a graduated flask and clock, all data was measured using a pH meter, a hydrometer and a pressure gauge.

Steady-State Option

The first set of reactions, following the precautionary flush of the reactor, were operated at steady-state in three trials at a constant pressure, all measured after 24 hours of production. At this time, the liquid product (which was dissolved in a flask of 250 mL) was transferred to a tall graduated cylinder and the liquid's specific gravity was measured using a hydrometer. For every 2.5 mL of ammonia added to the flask, the specific gravity is reduced 1 g/cm^3 – through experimentation, it was determined that the solution remains stable until dropping over three marks, assuring accuracy in the collected data. The pH of the water in the reactor was also measured recorded before and after each trial using a digital pH meter. While a constant pressure was maintained for the gaseous N_2 and H_2 feeds, the experiment was limited by the valves controlling their flow, which could not exceed a pressure of 8 atm.

Table 4.1: Results of steady-state trials

Trial	Temperature (°C)	Result (mL NH_3)
1	450	1.25
2	200	1.25
3	25	0

The result of each steady-state run is recorded in Table 4.1 above. In the first trial, operated at 450°C, the specific gravity of the stock water was measured initially at 96 marks and, after its 24 hour run, was reduced to 95.5 marks. With every 2.5 mL of ammonia resulting in a drop of one mark, the product solution is measured to contain 1.25 mL of ammonia. In the second trial, operated at 200°C under otherwise identical circumstances, the product measured a similar drop of one half of a mark, indicating a yield of 1.25 mL of ammonia after 24 hours of production. The final run, operated at 25°C, produced little or no ammonia and did not result in a change in specific gravity. The product flasks from the first and second trials both demonstrated a pH of 6.4, measured using a digital pH meter.

Batch Option

After the completion of all steady-state trials, the system was once again flushed and prepared for a series of batch reaction trials. These trials differed from the steady-state trials in that all reactants were fed into the system at once rather than being continuously fed, and the total product was measured within one hour, allowing the trials to be operated within the same day. In each trial, as the ammonia exited the reactor, the pressure gauge of the product stream was used to record exit pressure, and the pressure drop in the reaction was calculated by subtracting the exit pressure from the entering pressure. The ideal gas equation indicates that, at a constant temperature and volume, the pressure drop of a system is proportional to the number of moles.

Table 4.2: Results of batch trials

Trial	Temperature (°C)	Residence Time	Total yield mol%
1	450	30 seconds	2
2	200	1 hour	10
3	75	1 hour	1

Table 4.2 contains the results of each batch reaction trial. The first trial was monitored for over 30 minutes, no additional product was converted after the first 30 seconds due to the activation of the Fe catalyst at high temperatures. In that first trial, a pressure of 2% was calculated, indicating a 2% yield. The second (200°C) and third (75°C) trials demonstrated much slower reactions and, after one hour, displayed a pressure drop of 10% and 1%, respectively.

Following the completion of all trials, measurements and calculations, the data was analyzed and interpreted to determine whether this type of reaction, steady-state or batch, could potentially be used for commercial production if further developed. The conclusion had been made that this process could easily prove useful for supplementing ammonia production, even at a small scale. The batch trials measured product yields between 1% and 10% - with a yield of 10%, this process could be used in parallel with current ammonia production, increasing the standard 20% single-pass conversion to 30%.

Centrifugal Approach:

When considering alternative approaches to industrial ammonia production, a process' costs, yield and environmental impact are some of the most important factors. As a result of the rise in concern over limited resources, plants may need to raise ammonia prices to compensate for the increased cost of feedstock. However, alterations in the process could potentially lower the plant's capital costs and help avoid the need to increase prices. One innovative approach, outlined in Figures 4.3 and 4.4, aims to replace the membranes needed in the processes detailed in Chapters 2 and 3 with a centrifugal membrane. These processes, operated at industrial scale, require 200 WGS membranes at an average cost of $100,000 each.[25] This centrifugal approach requires only one centrifugal membrane, eliminating these membrane costs while also increasing yield. A diagram of the centrifugal membrane is shown in Figure 4.3:

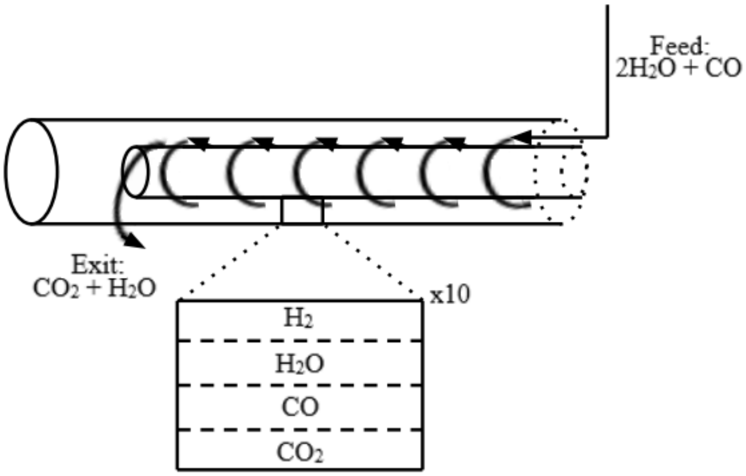


Figure 4.3: Diagram of Centrifugal Membrane

This process is designed to centrifugally separate gases in the membrane. With the use of a palladium-silver membrane for improved hydrogen separation, a centripetal feed forces the gases to separate in order of density, effectively isolating a stream of hydrogen (the lightest molecule present) while forcing heavier molecules through the membrane. This results in a boundary layer of pure hydrogen surrounding the membrane. In this design, isolated hydrogen provides better yields than the traditional feedstock of mixed H_2 and N_2, as demonstrated in the following calculations:

$Flux\ for\ pure\ hydrogen\ feed = \ 0.0015\ mol/sec$

$Flux\ for\ 50\%\ H2, 50\%\ N2\ mix = 0.00025 mol/sec$

$Relative\ efficacies = \frac{pure\ flux}{50/50\ flux} * 100\% = \mathit{600\%\ efficacy}$

The flux achieved with a feed of pure hydrogen, separated by a centrifugal membrane, could lead to yields six times as large as the current feedstock.**[14]**

The gases being forced through the membrane would be contained in a waste recovery system while the hydrogen stream would likely be fed through a compressor or heat exchanger, then into an ammonia reactor. If developed for commercial use, this centrifugal membrane process could replace the N_2 membranes used in current ammonia synthesis, reducing the plant's capital cost while operating at up to 600% efficacy.

Further development must be undergone before a prototype may be built. Hence, no qualitative data has been collected, leaving a number of questions that must be answered before the centrifugal membrane is scaled up for implementation. As with any piece of equipment, it is necessary to calculate or test the optimal flow rate for gas entering the centrifuge, as well as an optimal size proportional to that of the system. At this time, due to its current lack of association with ammonia manufacturing, it is still possible that the centrifugal membrane may be better applied elsewhere, in a different part of the process where it serves more useful. This project chose a centrifugal design for the separation of hydrogen feedstock due to its associated increase in flux and as an alternative to a costly current design, however, further alteration and experimentation may lead to a more practical use for this process.

It is predicted the use of a centrifugal membrane can potentially improve yield up to 600%, resulting in an obvious increase in supply and decrease in production costs. The substitution of a centrifugal membrane for the standard nitrogen membranes would also account for a lower capital cost, eliminating the need from 200 to about 34 membranes at a total cost of \$3.4 million instead of 20.

Chapter 5

Discussion, Conclusions and Recommended Future Research

Discussion:

In the interest of developing future options for ammonia production, this paper presents the current industrial process (discussed in Chapter 2) alongside the patented process designed for this project and discussed in Chapter 3, comparing the two methods in terms of their environmental impact and economic feasibility, as well as their effect on the cost of ammonia production and sales. Because the patented process in Chapter 3 has not yet been built, results concluding the production, cost and efficiency of a plant are based on simplified calculations, while results concerning the price and environmental impact of current ammonia production are found empirically.

According to the project advisor, additional factors must be taken into consideration to predict more accurate capital costs for the patented process: All capital costs recorded in Chapter 3 of this paper were calculated by the software Capcost based on the input of several variables. However, according to industry experts: Capcost is known to overvalue, and it is expected that the software consistently overestimates the cost of equipment by up to 30%. Software like Capcost is designed to predict the cost needed to build a plant and, because of the variety of equipment that displays a large price range, the software gives the highest estimated price to assure that this value could afford all capital costs. If the software calculated only average or lower prices, users would risk calculating a capital cost less than the actual cost, putting the plant's budget and expected profit in jeopardy. As a result, the $702 million fixed capital cost of the plant could in reality account for as little as $491.4 million. This reduction in capital costs would result in a break-even point at approximately 1.6 years of operation. According to the project advisor, commercial process designs estimated to reach a break-even point within two years are typically approved for implementation by commercial manufacturers with minimum review, due to optimization standards having already been achieved. Such processes are also highly profitable in commercial production compared to processes that require more time to break-even, paying off capital costs soon after the start of operation and turning a larger profit for each year that the process is used.

Chapter 4 of this paper concerns novel ideas and approaches designed to increase the yield and efficiency of commercial ammonia synthesis. The first approach involved coupling the WGS reaction and ammonia synthesis reaction used in the processes described in Chapters 2 and

3, conducting both within a closed, heated vessel and allowing the hydrogen released in the WGS reaction to serve as feedstock for ammonia synthesis, while the second approach involved the use of a centrifugal membrane, intended to reduce membrane costs and increase yield. The former approach has been demonstrated to improve yield in ammonia synthesis, though further optimization is necessary before this approach can be modeled or constructed for commercial use. The latter approach is calculated to increase yield by up to 600%, though without a functioning prototype, this claim cannot be verified.

Conclusion:

Through extensive research and calculation, the processes described in Chapters 2 and 3 were analyzed and compared based on their associated costs, production value and environmental impact. The results produced throughout the project indicate that the process illustrated in Chapter 3 is less expensive and more environmentally responsible than current ammonia synthesis processes. The current process described in Chapter 2 has an affiliated production cost of $600 per ton of ammonia, resulting in a break-even point after approximately five years. The patented process from Chapter 3, however, is expected to reach a break-even point after less than two years of operation, with an affiliated production cost of $232 of per ton. The present value for the plant detailed in Chapter 3 is $5.33 billion with a calculated ROI of 223%. It has been predicted that, if the patented process were used to replace current processes for ammonia synthesis, the change could account for a 7% reduction in global greenhouse gas emissions.

The results of Chapter 4 provide direction for research regarding the optimization of future ammonia and fertilizer production, indicated in the Recommended Future Research section of this chapter.

Recommended Future Research:

The technology mentioned in Chapter 3 can be directly implemented to industry; proper data and experimentation were run on the suggested technologies. However, Chapter 4 recommends that a number of recently-developed techniques and industrial processes be integrated into commercial ammonia synthesis, further research, modelling and experimentation are needed before successful implementation can be achieved. Steps that can be taken to further pursue the methods discussed in this paper are included in the following recommendations:

- Optimize flow conditions and design for centrifugal membrane design.
- Optimize conditions for the coupled WGS and NH_3 synthesis reactions to achieve best yield.
- Consider the low-pressure reaction of ammonia synthesis for additional 10% single-pass conversion (discussed briefly in Chapter 4).
- Couple the production of ammonia with that of urea to increase efficiency and reduce the emission of greenhouse gases.
- Research the effects of water dependence on ammonia synthesis compared to the effects of natural gas dependence if scaled for global production.
- Thoroughly assess the environmental impact of water-dependent ammonia production at a global scale.

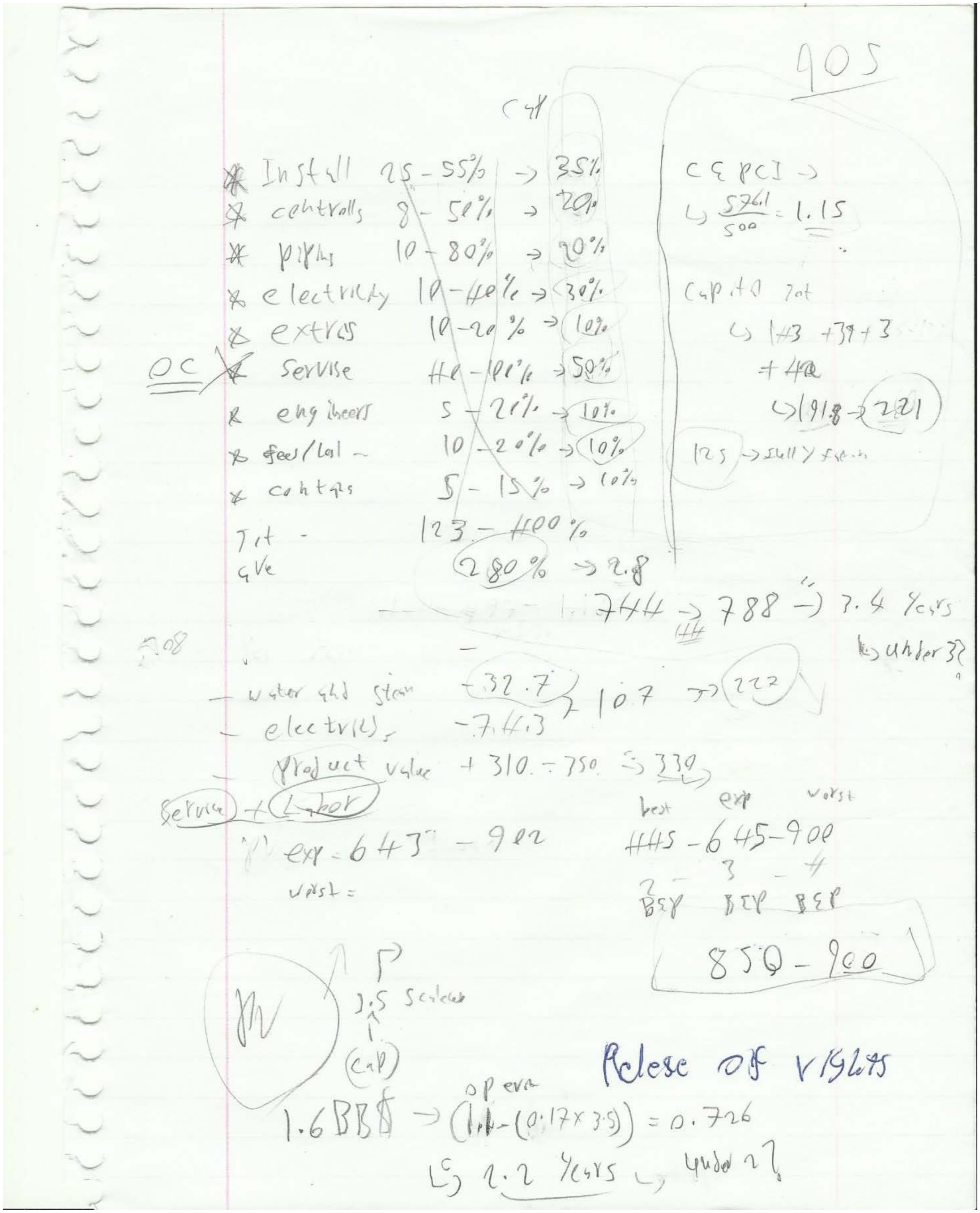
References:

1. Chavis, Jason C. "The Effects and Uses of Ammonia in Agriculture." 4 June 2014. Web. 22 May 2015. <http://www.brighthub.com/environment/science-environmental/articles/73262.aspx>.
2. Roper, L. David. "World Ammonia Production." 11 Jan. 2015. Web. 17 May 2015. <http://www.roperld.com/science/minerals/ammonia.htm>.
3. Vroomen, Harry. "Natural Gas and the U.S. Fertilizer Industry." 15 July 2010. Web. 17 May 2015. <http://consumerenergyalliance.org/wp/wp-content/uploads/2010/07/Vroomen-CEA-Natural-Gas-Committee-July-15-2010-presentation-at-TFI-hv.pdf>.
4. Ball, Jeff. "Back to Basics: The Roles of N, P, K and Their Sourced." Jan. 2007. Web. 22 May 2015. <http://www.noble.org/ag/soils/back2basics/>.
5. "Fertilizer Requirements in 2015 and 2030." Rood and Agriculture Organization of the United Nations, 2000. Web. 10 May 2015. <ftp://ftp.fao.org/agl/agll/docs/barfinal.pdf>.
6. United States. Environmental Protection Agency. *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2012*. 15 Apr. 2014. Web. 23 May 2015. < ftp://ftp.fao.org/agl/agll/docs/barfinal.pdf >.
7. Van Der Ploeg, R. R., W. Bohm, and M. B. Kirkham. "History of Soil Science: On the Origin of the Theory of Mineral Nutrition of Plants and the Law of the Minimum." Web. 17 May 2015. <http://academic.uprm.edu/dsotomayor/agro6505/VanderPloeg_etal_sssaj_Sprengel-Liebegpdf.pdf>.
8. Almqvist, Ebbe. *History of Industrial Gases*. New York, NY: Kluwer Academic/Plenum, 2003. 83
9. Erisman, Jan Willem, Mark A. Sutton, Zbigniew Klimont, and Wilfried Winiwarter. "How a Century of Ammonia Synthesis Changed the World." *Nature Geoscience*. 2008. Web. 17 May 2015. <http://www.nature.com/ngeo/journal/v1/n10/full/ngeo325.html>.
10. Himstedt, Heath, Alon V. McCormick, and Edward L. Cussler. "Small-Scale Production of Ammonia From a Combined Reactor-Membrane-Adsorber." 8 Nov. 2013. Web. 24 May 2015. <https://aiche.confex.com/aiche/2013/webprogram/Paper325135.html>.

11. Smil, Vaclav. "Detonator of the Population Explosion." 1997. Web. 22 May 2015. <http://www.vaclavsmil.com/wp-content/uploads/docs/smil-article-1999-nature7.pdf>.
12. Ruder, Jon, and Edwin Bennion. "Growing Demand for Fertilizer Keeps Prices High." May 2013. Web. 23 May 2015. <http://www.bls.gov/opub/btn/volume-2/growing-demand-for-fertilizer-keeps-prices-high.htm>.
13. Overmann, Stephen R. "Water Pollution by Agricultural Chemicals." Southeast Missouri State University, 2001. Web. 1 June 2015. <http://wps.prenhall.com/wps/media/objects/1027/1052055/Regional_Updates/update30.htm>.
14. Catalano, Jacopo, Federico Guazzone, Ivan P. Mardilovich, Nikolaos K. Kazantzis, and Yi Hua Ma. *Hydrogen Production in a Large Scale Water-Gas Shift Pd-Based Catalytic Membrane Reactor*. Worcester Polytechnic Institute, 21 Dec. 2011. Web. 2 Apr. 2015. <http://pubs.acs.org/doi/abs/10.1021/ie2025008>.
15. United States. Environmental Protection Agency. Technical Support Division.*Background Report AP-42 Section 5.2: Synthetic Ammonia*. Research Triangle Park, NC
16. *Process Flow Diagram of Ammonia Production*. Web. 15 Aug. 2015. <http://www.magicrot.ru/index.php?p=AmmoniaProduction&LANG_=ENG>.
17. Schnitkey, Gary. "Monthly Fertilizer Prices: Spring 2014 with Comparisons to 2009 through 2013." University of Illinois at Urbana-Champaign, 15 Apr. 2014. Web. 28 May 2015. <http://farmdocdaily.illinois.edu/2014/04/monthly-fertilizer-prices-spring2014-with-comparisons.html>.
18. Incitec Pivot Limited. *Louisiana Ammonia Plant*. Dyno Nobel, 17 Apr. 2013. Web. 4 Aug. 2015. <http://www.asx.com.au/asxpdf/20130417/pdf/42f9brx9b4xscx.pdf>.
19. Vorotto, Alessandro, PhD. "Raising the Standards: Enhanced Catalytic Performance for Global Ammonia Production." Quantumsphere. Web. 31 May 2015. <http://qsinano.com/wp-content/uploads/2014/08/QSI-Ammonia-Whitepaper-FINAL-12-Aug-14.pdf>.
20. United States. Environmental Protection Agency. Office of Air Quality. *Compilation of Air Pollutant Emission Factors*. Jan. 1995. Web. 31 May 2015. <http://www.epa.gov/ttnchie1/ap42/ch06/final/c06s01.pdf>.

21. Seider, Warren D., J. D. Seader, Daniel R. Lewin, and Soemantri Widagdo. *Product and Process Design Principles: Synthesis, Analysis, and Evaluation*. Hoboken, NJ: Wiley & Sons, 2010.
22. Thompson, Edward V., and William H. Ceckler. *Introduction to Chemical Engineering*. New York, NY: McGraw-Hill, 1977.
23. "Costs of Doing Business." *Saudi Arabian General Investment Authority*. 2015. Web. 27 June 2015. <https://www.sagia.gov.sa/en/Investment-climate/Costs-Of-Doing-Business/>.
24. "Kingdom of Saudi Arabia Electricity Tariffs." Dynamic Energy and Water Solutions. Web. 27 June 2015. <http://www.dynamic-ews.com/Tariffs/Electricity%20Tariffs/KSA.pdf>.
25. AIChE. "2015 AIChE Salary Survey." *Chemical Engineering Progress* June 2015: 15-21.
26. Ma, Liang-Chih, Bernardo Castro-Dominguez, Nikolaos K. Kazantzis, and Yi Hua Ma. *Integration of Membrane Technology into Hydrogen Production Plants With CO2 Capture: An Economic Performance Assessment Study*. Tech. Worcester, MA: Worcester Polytechnic Institute, 2015.
27. "Global Carbon Emissions." *CO2 Now*. 21 Sept. 2014. Web. 8 Aug. 2015. <http://co2now.org/Current-CO2/CO2-Now/global-carbon-emissions.html>.

Appendix A.1



905

Cost

Install 25 - 55% → 35%
controlls 8 - 50% → 20%
piping 10 - 80% → 70%
electricity 10 - 40% → 30%
extras 10 - 20% → 10%
OC ~~service~~ 40 - 100% → 50%
engineers 5 - 20% → 10%
fees/lab 10 - 20% → 10%
contigs 5 - 15% → 10%
Tot - 123 - 400%
ave 280% → 2.8

CE PCI →
↳ 576.1 / 500 = 1.15

Capital Tot
↳ 143 + 39 + 3 + 40
↳ 191.8 → 221

125 → sully fresh

744 → 788 → 3.4 Years
↳ under 3?

208

- water and steam - 32.7
- electricity - 74.3
} 107 → 222
- product value + 310 - 750 → 330

Service + Labor
exp - 643 - 900
worst =

best exp worst
445 - 645 - 900
2 - 3 - 4
BEP BEP BEP

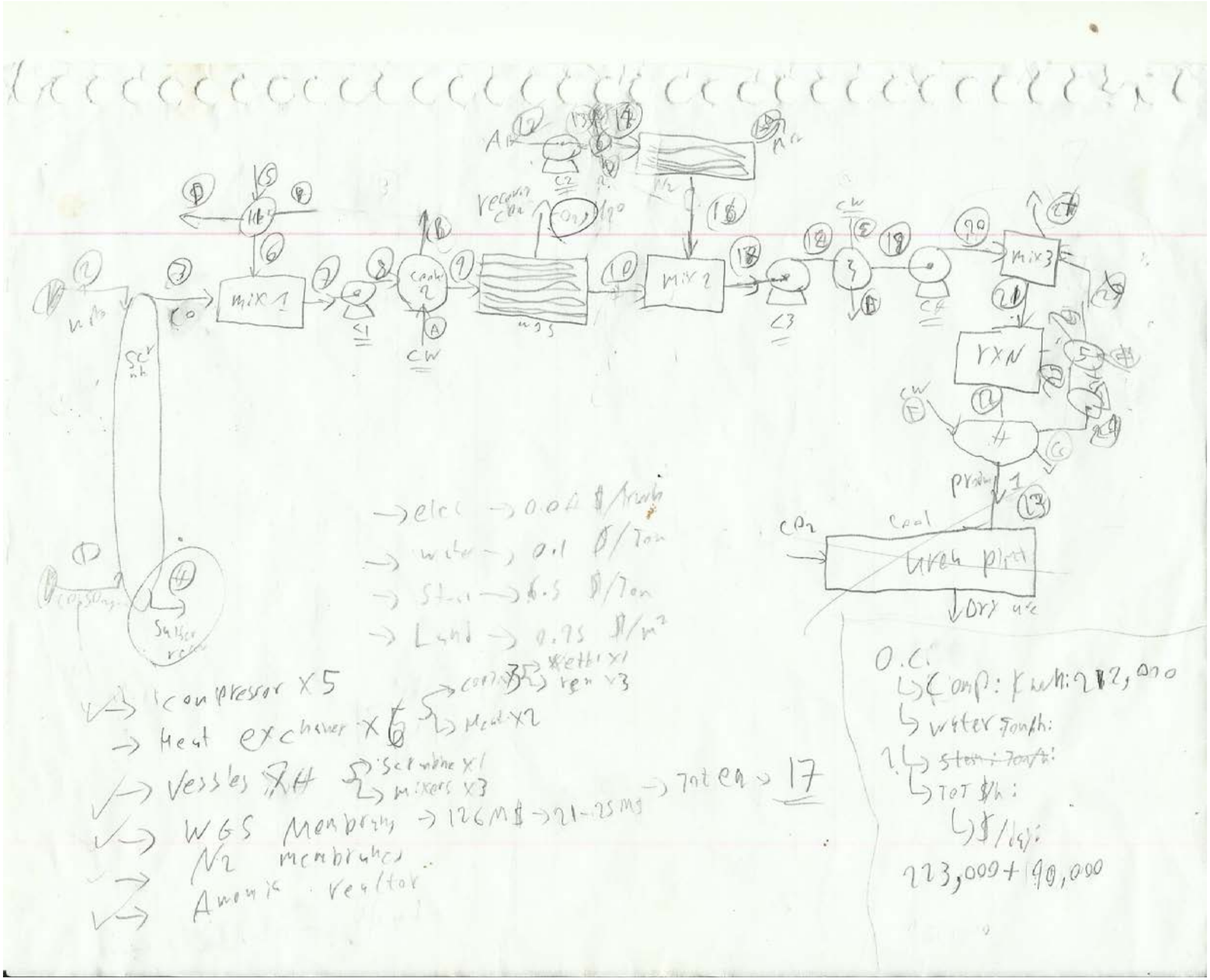
850 - 900

1.5 Scale
(cap)

Relese of rights

op erra
1.6 BB$ → (1.4 - (0.17 × 3.5)) = 0.726
↳ 2.2 Years ↳ under 2?

Appendix A.2

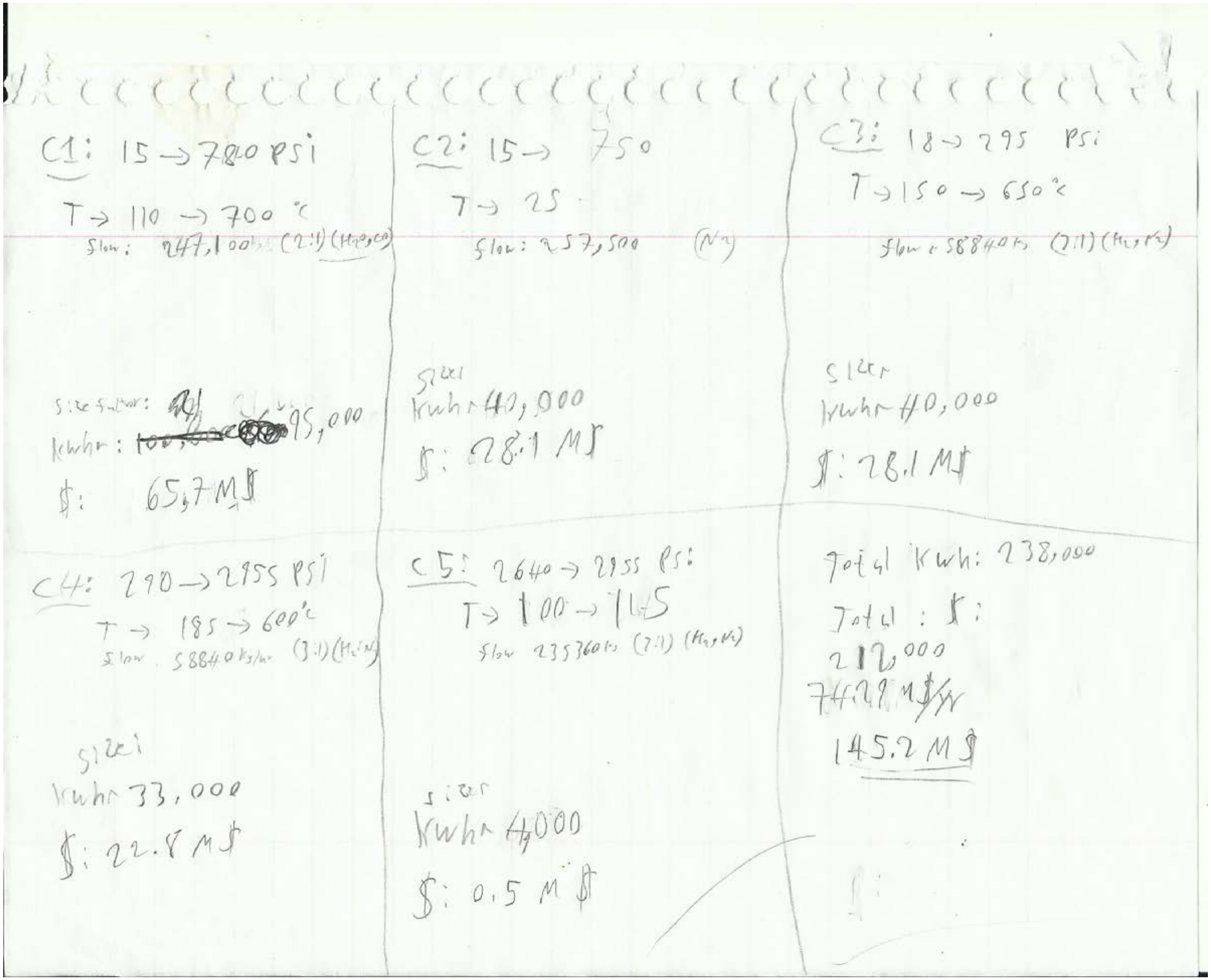


→ elec → 0.04 $/kwh
→ water → 0.1 $/Ton
→ Steam → 6.5 $/Ton
→ Land → 0.75 $/m²

✓→ compressor X5
→ Heat exchanger X6 → cond. X3 → kettle X1, → ren X3; → Heat X2
✓→ Vessles X4 → scrubber X1, → mixers X3 → Tot eq → 17
✓→ WGS Membrane → 126M$ → 21-25M$
→ N2 membranes
✓→ Ammonia reactor

O.C.
↳ Comp: kwh: 282,000
↳ water Ton/h:
?↳ ~~Steam: Ton/h~~:
↳ TOT $/h:
↳ $/day:
223,000 + 90,000

Appendix A.3



C1: 15 → 780 psi
T → 110 → 700 °C
flow: 247,100 lbs (2:1) (H_2O, CO)

Size factor: [illegible]
kwhr: ~~100,000~~ 95,000
$: 65.7 M$

C4: 290 → 2955 psi
T → 185 → 600 °C
flow 58840 kg/hr (3:1) $(H_2:N_2)$

size:
kwhr 33,000
$: 22.8 M$

C2: 15 → 750
T → 25
flow: 257,500 (N_2)

size:
kwhr 40,000
$: 28.1 M$

C5: 2640 → 2955 psi
T → 100 → 145
flow 235360 kg (7:1) (H_2, N_2)

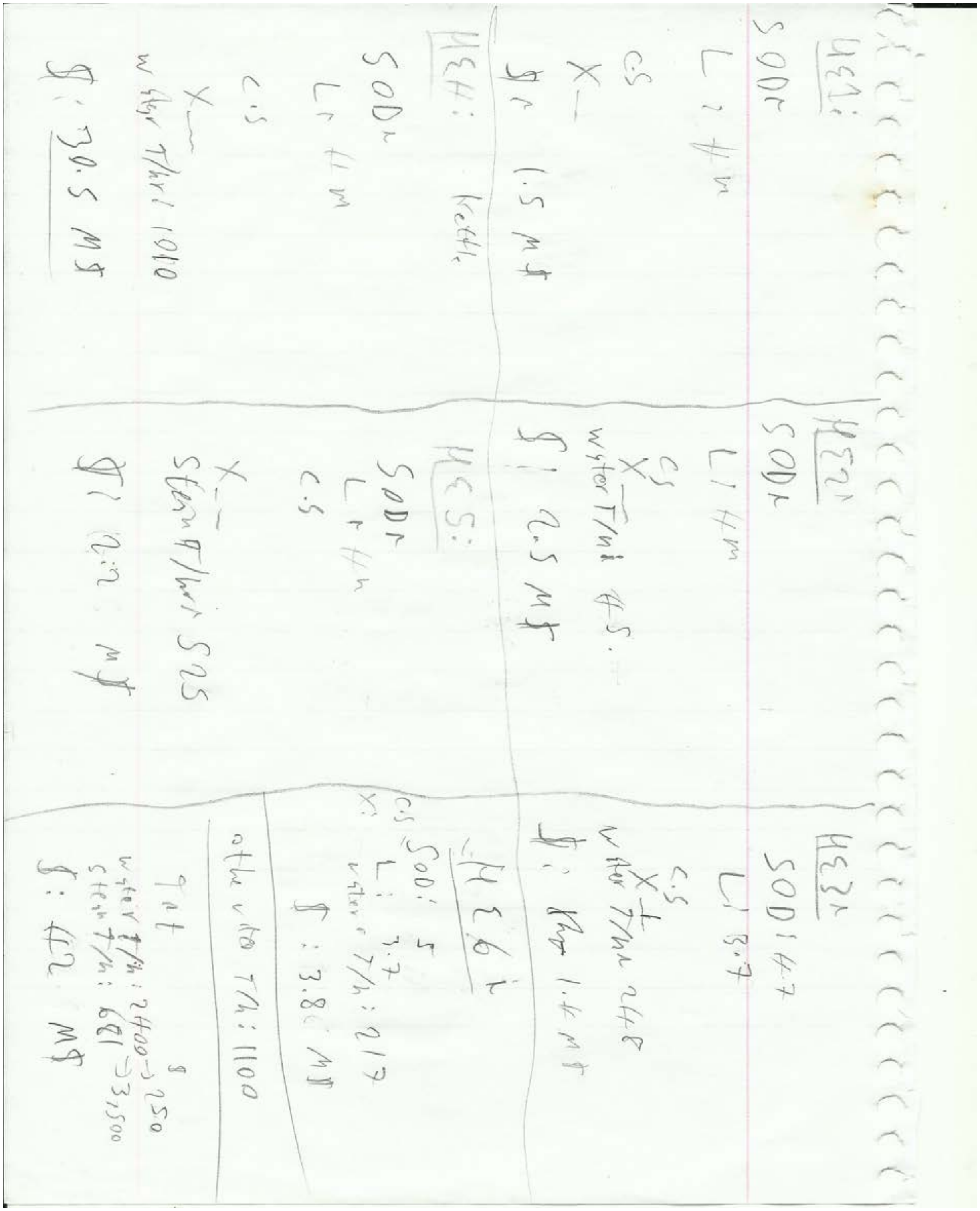
size:
kwhr 4000
$: 0.5 M$

C3: 18 → 295 psi
T → 150 → 650 °C
flow: 58840 kg (2:1) (H_2, N_2)

size:
kwhr 40,000
$: 28.1 M$

Total kwh: 238,000
Total: $:
212,000
74.29 M$/yr
145.2 M$

Appendix A.4



HE1:
SODr
L: 4 m
c.s
X_
$: 1.5 M$

HE2:
SOD:
L: 4 m
c.s
X_
water T/hr: 45.
$: 2.5 M$

HE3:
SOD: 4.7
L: 3.7
c.s
X 1
water T/hr 248
$: 1.4 M$

HE4: kettle
SOD:
L: 4 m
c.s
X_
water T/hr: 1010
$: 30.5 M$

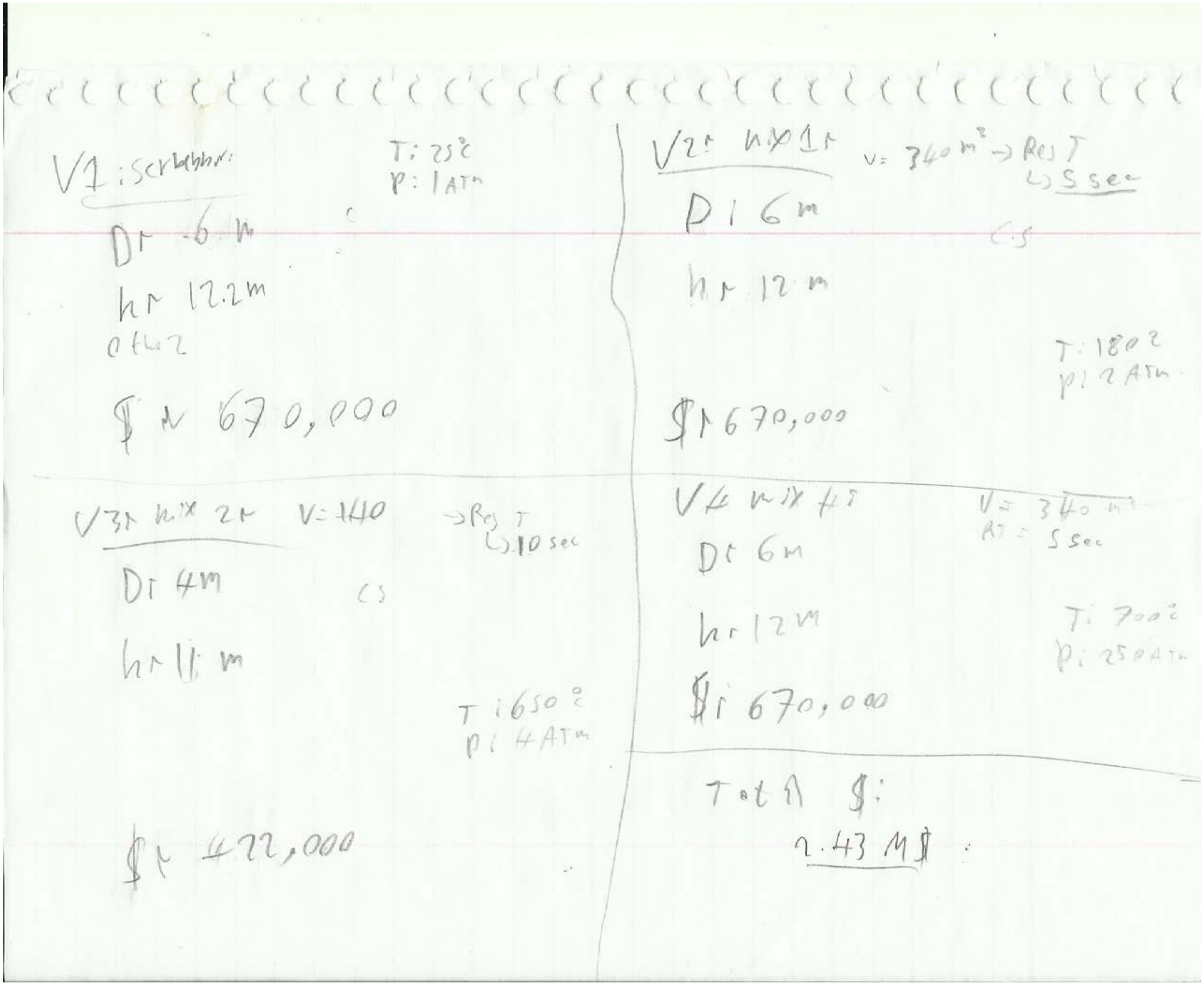
HE5:
SOD:
L: 4 h
c.s
X_
steam T/hr: 525
$: 2.2 M$

HE6:
c.s SOD: 5
L: 3.7
X: water T/h: 217
$: 3.8 M$

other water T/h: 1100

Tot
$
water T/h: 2400 → 250
steam T/h: 681 → 3,500
$: 42 M$

Appendix A.5



V1: scrubber:
T: 25°C
P: 1ATM

D: 6 m

h: 12.2m

other

$: 670,000

V2: mix 1:
V= 340 m³ → Res T
↳ 5 sec

D: 6m

C.S

h: 12 m

T: 180°C
P: 2 ATM

$: 670,000

V3: mix 2: V= 140
→ Res T
↳ 10 sec

D: 4m

CS

h: 11 m

T: 650°C
P: 4 ATM

$: 422,000

V4 mix 4:
V= 340 m³
RT = 5 sec

D: 6m

h: 12m

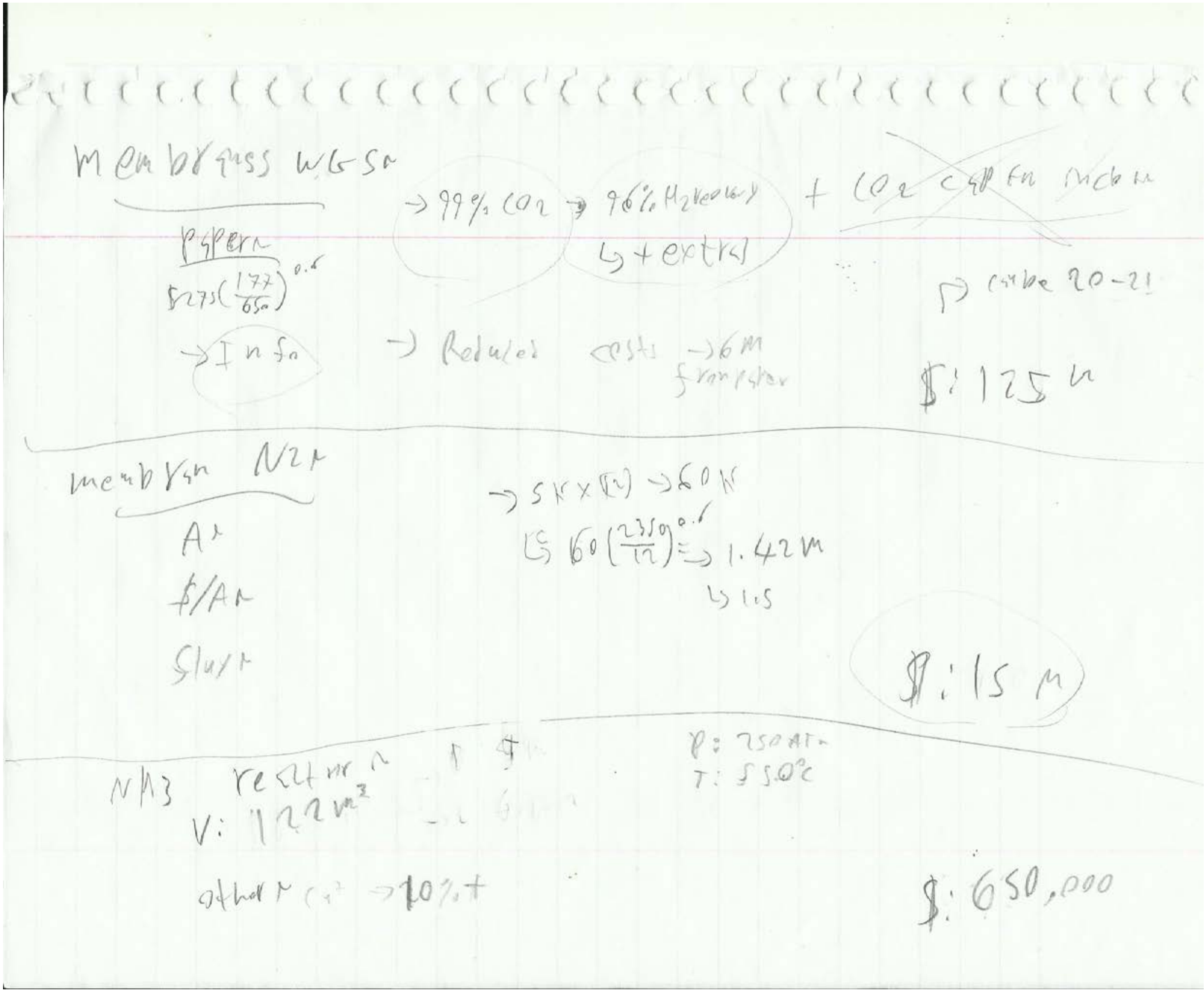
T: 700°C
P: 250 ATM

$: 670,000

Total $:

2.43 M$

Appendix A.6



Membranes w/ GSR

Papers

$275\left(\frac{177}{650}\right)^{0.6}$

→ Info

→ 99% CO2 → 96% H2 recovery

↳ + extra

+ ~~CO2 capture mechanism~~

↳ carbon 20-21

→ Reduced costs → 6M
from paper

$: 125 M

Membrane N2

Area

$/Area

Sizer

→ 5k × (12) → 60k

↳ $60\left(\frac{2350}{12}\right)^{0.6} \Rightarrow 1.42M$

↳ 1.5

$: 15 M

NH3 reactor

V: 122 m³

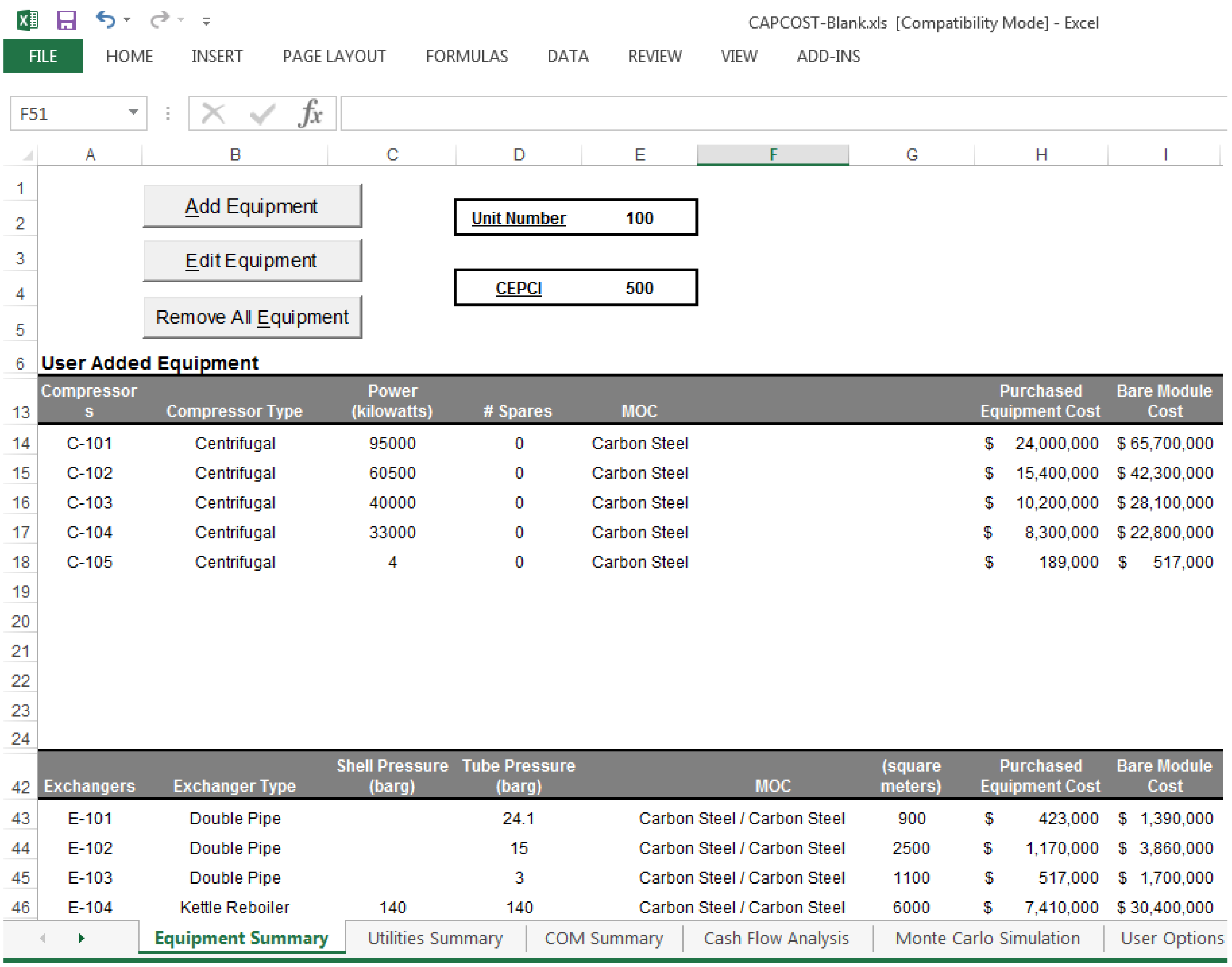
P: 250 atm

T: 550°C

other r(x) → 10% +

$: 650,000

Appendix B.1



Unit Number 100

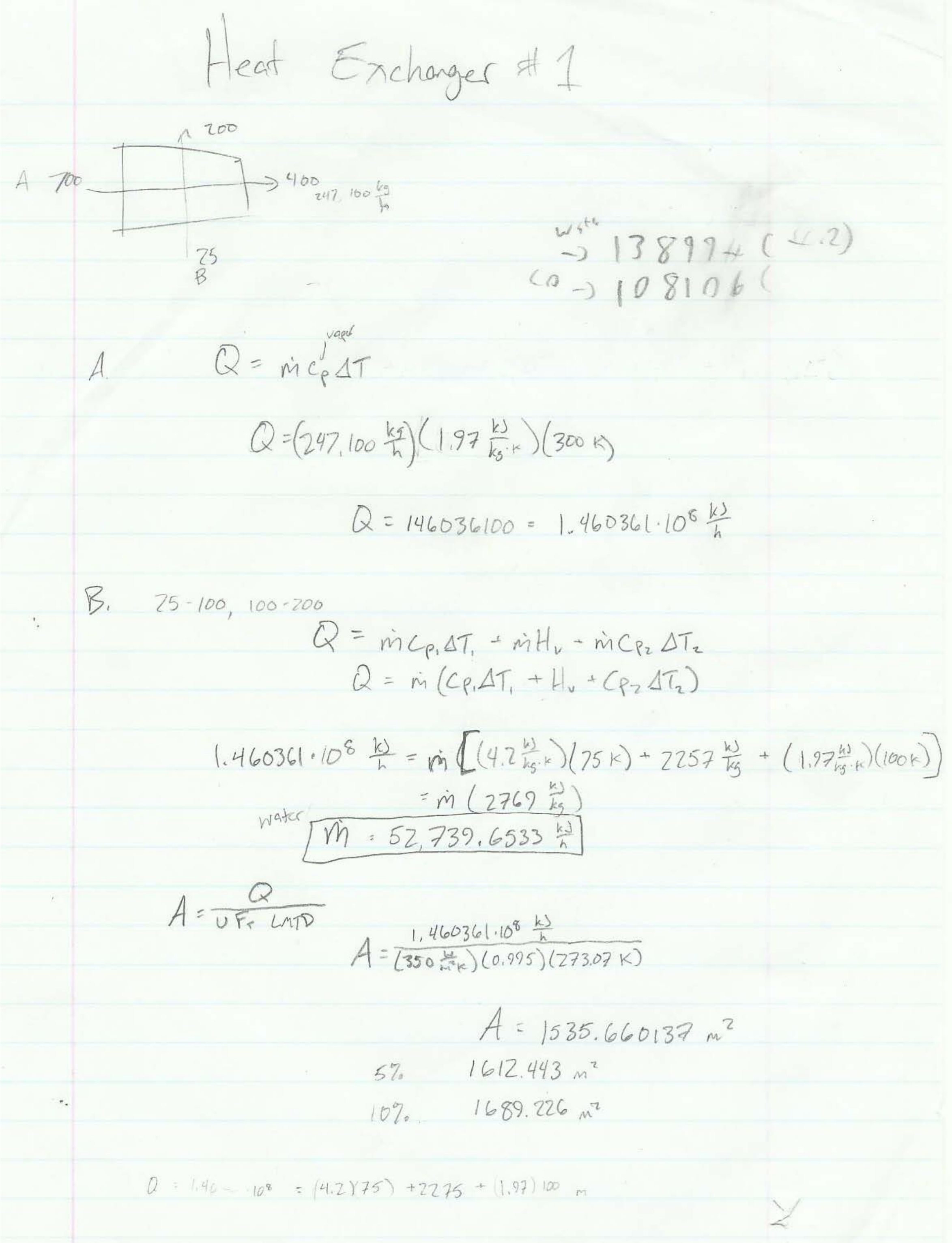
CEPCI 500

User Added Equipment

Compressors	Compressor Type	Power (kilowatts)	# Spares	MOC	Purchased Equipment Cost	Bare Module Cost
C-101	Centrifugal	95000	0	Carbon Steel	$ 24,000,000	$ 65,700,000
C-102	Centrifugal	60500	0	Carbon Steel	$ 15,400,000	$ 42,300,000
C-103	Centrifugal	40000	0	Carbon Steel	$ 10,200,000	$ 28,100,000
C-104	Centrifugal	33000	0	Carbon Steel	$ 8,300,000	$ 22,800,000
C-105	Centrifugal	4	0	Carbon Steel	$ 189,000	$ 517,000

Exchangers	Exchanger Type	Shell Pressure (barg)	Tube Pressure (barg)	MOC	(square meters)	Purchased Equipment Cost	Bare Module Cost
E-101	Double Pipe		24.1	Carbon Steel / Carbon Steel	900	$ 423,000	$ 1,390,000
E-102	Double Pipe		15	Carbon Steel / Carbon Steel	2500	$ 1,170,000	$ 3,860,000
E-103	Double Pipe		3	Carbon Steel / Carbon Steel	1100	$ 517,000	$ 1,700,000
E-104	Kettle Reboiler	140	140	Carbon Steel / Carbon Steel	6000	$ 7,410,000	$ 30,400,000

Appendix B.2



Heat Exchanger #1

wster → 138997 (4.2)
Co → 108106 (

A. $Q = \dot{m}\overset{\text{vapd}}{c_p}\Delta T$

$Q = (247{,}100 \frac{kg}{h})(1.97 \frac{kJ}{kg \cdot K})(300\ K)$

$Q = 146036100 = 1.460361 \cdot 10^8 \frac{kJ}{h}$

B. 25-100, 100-200

$Q = \dot{m}C_{p_1}\Delta T_1 + \dot{m}H_v + \dot{m}C_{p_2}\Delta T_2$

$Q = \dot{m}(C_{p_1}\Delta T_1 + H_v + C_{p_2}\Delta T_2)$

$1.460361 \cdot 10^8 \frac{kJ}{h} = \dot{m}\left[(4.2 \frac{kJ}{kg \cdot K})(75\ K) + 2257 \frac{kJ}{kg} + (1.97 \frac{kJ}{kg \cdot K})(100\ K)\right]$

$= \dot{m}(2769 \frac{kJ}{kg})$

water $\boxed{\dot{m} = 52{,}739.6533 \frac{kJ}{h}}$

$A = \frac{Q}{U F_T\ LMTD}$

$A = \frac{1.460361 \cdot 10^8 \frac{kJ}{h}}{(350 \frac{kJ}{m^2 K})(0.995)(273.07\ K)}$

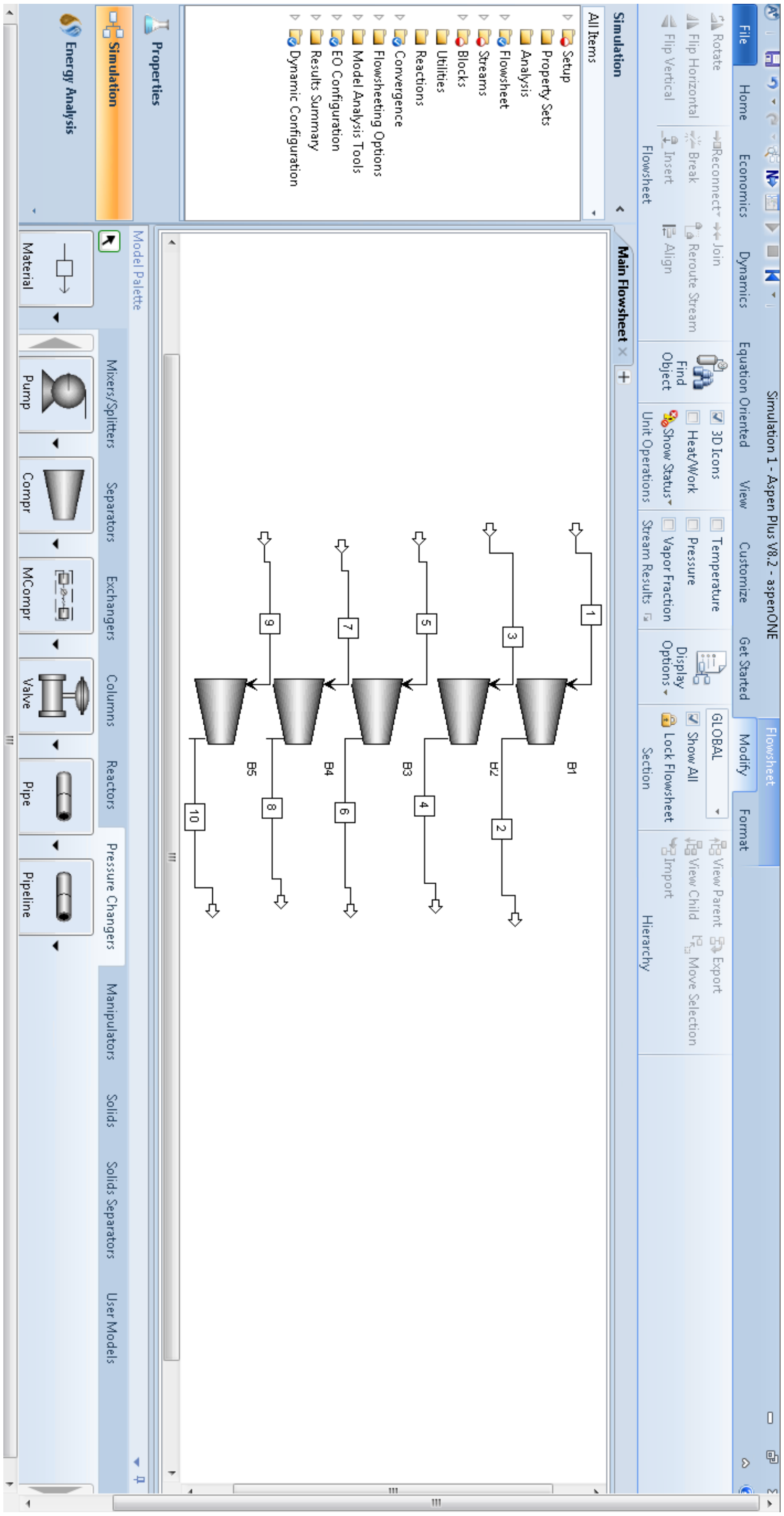
$A = 1535.660137\ m^2$

5% 1612.443 m^2

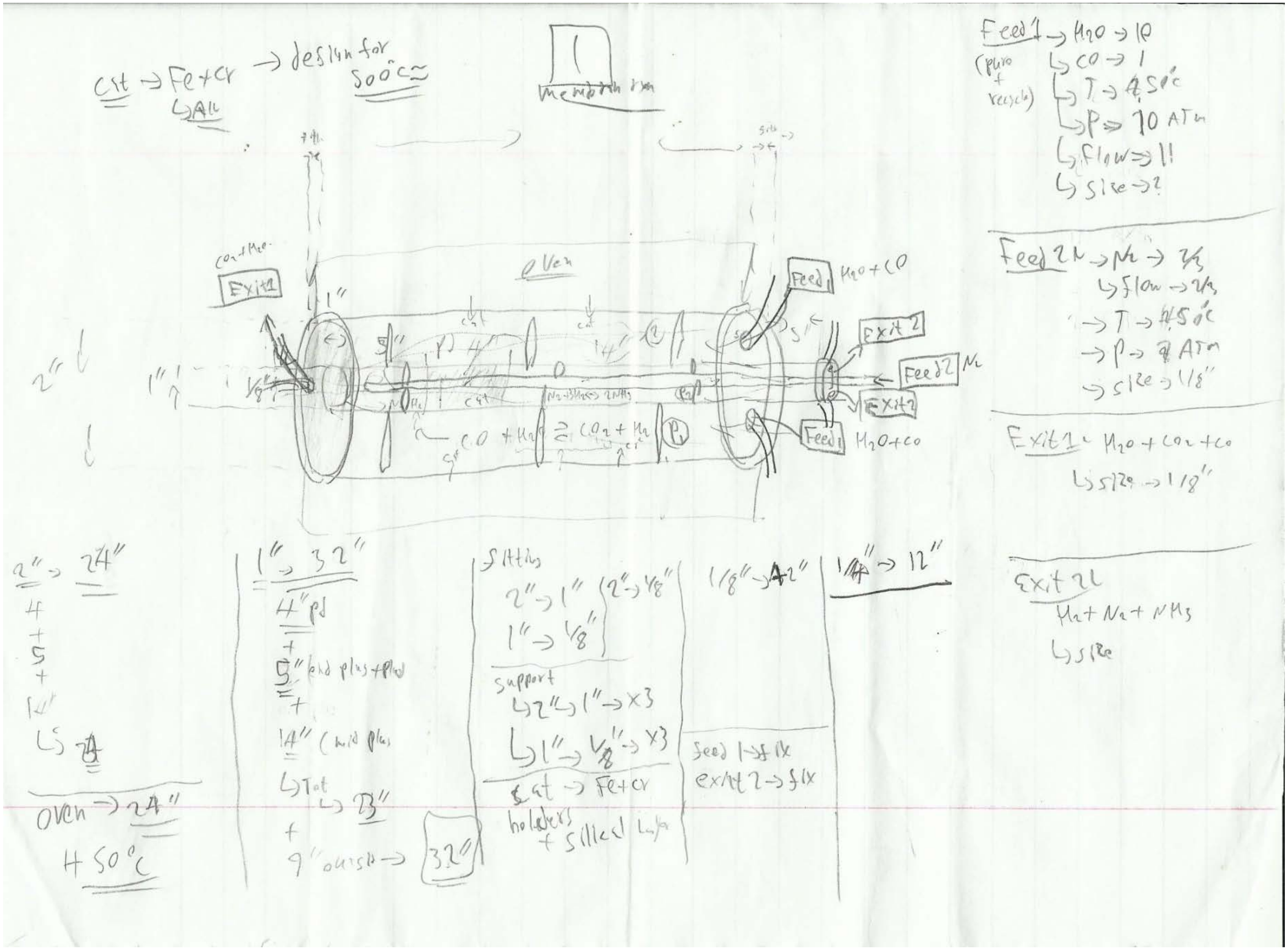
10% 1689.226 m^2

$Q = 1.46 \cdot 10^8 = (4.2)(75) + 2275 + (1.97)100\ m$

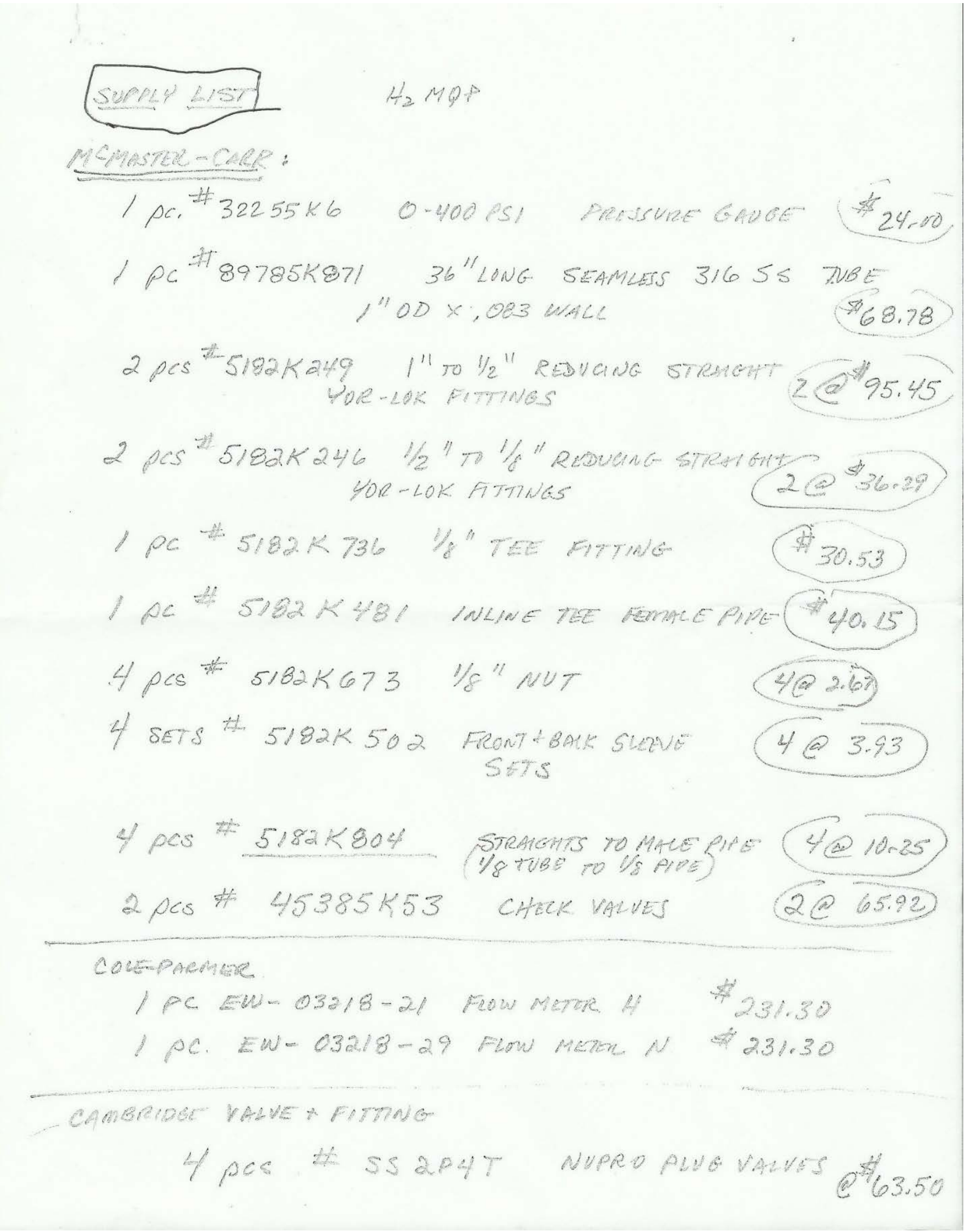
Appendix B.3


Simulation 1 - Aspen Plus V8.2 - aspenONE
File
Home
Economics
Dynamics
Equation Oriented
View
Customize
Get Started
Flowsheet
Modify
Format
Rotate
Flip Horizontal
Flip Vertical
Reconnect
Break
Insert
Join
Reroute Stream
Align
Flowsheet
Find Object
3D Icons
Heat/Work
Show Status
Unit Operations
Temperature
Pressure
Vapor Fraction
Stream Results
Display Options
GLOBAL
Show All
Lock Flowsheet
Section
View Parent
View Child
Import
Export
Move Selection
Hierarchy
Simulation
All Items
Setup
Property Sets
Analysis
Flowsheet
Streams
Blocks
Utilities
Reactions
Convergence
Flowsheeting Options
Model Analysis Tools
EO Configuration
Results Summary
Dynamic Configuration
Properties
Simulation
Energy Analysis
Main Flowsheet
1
2
3
4
5
6
7
8
9
10
B1
B2
B3
B4
B5
Model Palette
Mixers/Splitters
Separators
Exchangers
Columns
Reactors
Pressure Changers
Manipulators
Solids
Solids Separators
User Models
Material
Pump
Compr
MCompr
Valve
Pipe
Pipeline

Appendix C


Cat → Fe+Cr → design for 500°C≈
↳ All
membrane
Feed 1 → H2O → 10
(pure + recycle)
↳ CO → 1
↳ T → 450°C
↳ P → 10 ATm
↳ flow → 11
↳ size → ?
Feed 2 → N2 → 2/3
↳ flow → 2/3
→ T → 450°C
→ P → 9 ATm
→ size → 1/8"
Exit 1 H2O + CO2 + CO
↳ size → 1/8"
Exit 2 H2 + N2 + NH3
↳ size
CO2+H2O
Exit 1
oven
1"
1/8"
5"
4"
cat
14"
N2+3H2 ⇌ 2NH3
CO + H2O ⇌ CO2 + H2
P1
P2
Feed 1 H2O + CO
Exit 2
Feed 2 N2
Exit 2
Feed 1 H2O+CO
5"
2"
1"
2" → 24"
4
+
5
+
14"
↳ 24
oven → 24"
+ 50°C
1" → 32"
4" pd
+
5" end plus + plug
+
14" (mid plus
↳ Tot
↳ 23"
+
9" outside → 32"
fitting
2" → 1"
1" → 1/8"
(2" → 1/8"
support
↳ 2" ↳ 1" → x3
↳ 1" → 1/8" → x3
cat → Fe+Cr
holders
+ silled
1/8" → 42"
feed 1 → fix
exit 2 → fix
1/4" → 12"

Appendix D



SUPPLY LIST H_2 MQP

MCMASTER-CARR:

1 pc.	# 32255K6	0-400 PSI PRESSURE GAUGE	$24.00
1 pc	# 89785K871	36" LONG SEAMLESS 316 SS TUBE 1" OD X .083 WALL	$68.78
2 pcs	# 5182K249	1" TO 1/2" REDUCING STRAIGHT YOR-LOK FITTINGS	2 @ $95.45
2 pcs	# 5182K246	1/2" TO 1/8" REDUCING STRAIGHT YOR-LOK FITTINGS	2 @ $36.29
1 pc	# 5182K736	1/8" TEE FITTING	$30.53
1 pc	# 5182K481	INLINE TEE FEMALE PIPE	$40.15
4 pcs	# 5182K673	1/8" NUT	4 @ 2.67
4 SETS	# 5182K502	FRONT + BACK SLEEVE SETS	4 @ 3.93
4 pcs	# 5182K804	STRAIGHTS TO MALE PIPE (1/8 TUBE TO 1/8 PIPE)	4 @ 10.25
2 pcs	# 45385K53	CHECK VALVES	2 @ 65.92

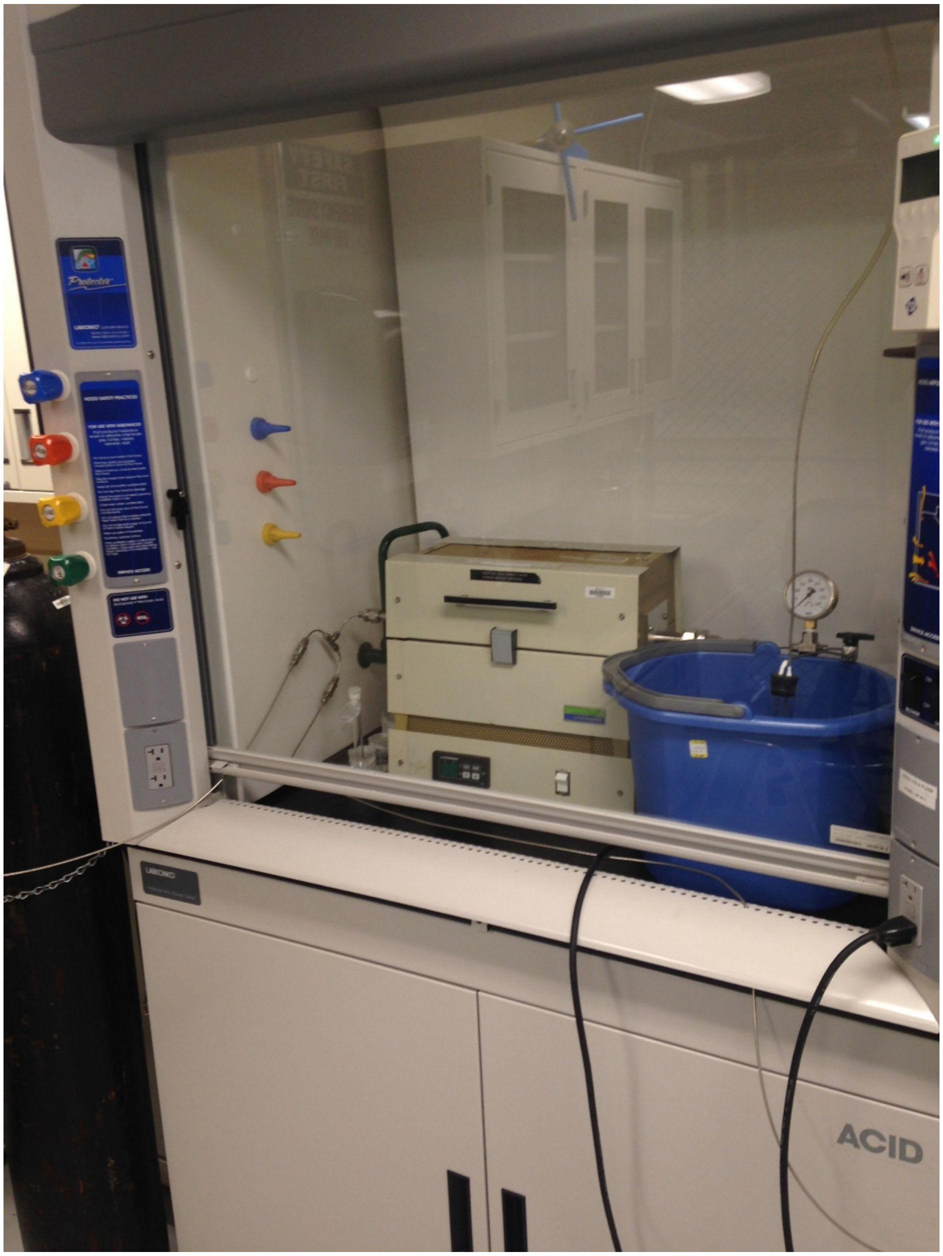
COLE-PARMER

1 PC	EW-03218-21	FLOW METER H	$231.30
1 pc.	EW-03218-29	FLOW METER N	$231.30

CAMBRIDGE VALVE + FITTING

4 pcs	# SS 2P4T	NUPRO PLUG VALVES	@ $63.50

Appendix E


ACID


SHUT
THE
SASH
THANKS
ENERGY
ACID


50
100
150
200
250
300
350
400
psi
Snoo
LINDBERG