Carbon-Neutral Production Of Methanol Via Direct Air Carbon Capture

A Technical Report submitted to the Department of Chemical Engineering

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On my honor as a University Student, I have neither given nor received unauthorized aid on this assignment as defined by the Honor Guidelines for Thesis-Related Assignments

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SUMMARY

Rapid changes in weather and environmental conditions due to the effects of climate change have created the necessity to reevaluate industrial societies and their carbon emitting practices. It is reported that in order to prevent global warming beyond two-degree Celsius, the target set out by the Paris Climate agreement, adjusting manufacturing practices and energy sources to approach net carbon-neutrality is not sufficient. Instead, developing carbon-negative technologies, like direct air carbon capture, is necessary (Wilcox, 2021). However, the end use of captured carbon needs to be considered as it is typically considered a waste molecule.

In this report, a direct air carbon capture system is designed alongside a methanol production plant with the goal of capturing and utilizing ambient carbon dioxide. In a seven unit system, air is captured via an Air Contactor where 1.8 trillion kg/year of air is processed and residing carbon dioxide is absorbed in an aqueous sorbent. After the carbon dioxide is extracted from the air, it is sent through a calcium caustic loop and calcium carbonate regeneration system consisting of a Pellet Reactor, Calciner, and Slaker. A purified stream of carbon dioxide (99.8%) leaving the Calciner is produced at 1.2 billion kg/year, with 0.97 billion kg/year of carbon dioxide being extracted from the atmosphere and the remaining carbon dioxide being produced from a required combustion reaction taking place.This purified stream is then sent to the Reverse Water Gas Shift Reactor to produce a carbon monoxide stream. This is then followed by a Methanol Synthesis Reactor where the carbon monoxide is converted to methanol. A distillation column purifies the methanol stream, yielding product methanol of 99.9% with accurate material balances at a capacity of 820 million kg/year with a production schedule of 6000 hours/year.

Economic analysis of the plant design is hopeful, but requires additional work for it to become fully viable. With a calculated capital cost of $2 billion and yearly operational cost of $400 million, the DAC to methanol synthesis plant will produce $570 million in annual revenue. From this, an IRR of 1.47% can be understood. While the IRR is positive, it is not yet to the level needed in order for the project to be recommended. Though, with adjustments to the base design, the outlook of this plant could be improved. For example, methanol is currently sold at $659 per metric tonne; if the project's clean methanol is sold at a premium, the IRR rises significantly, indicating a lucrative design.

This design has a number of safety, environmental, and social considerations. The main safety concerns involve waste water streams and mechanical conveyors that pose a hazard to operators should any accidents occur. The environmental impact of this project is beneficial considering the amount of carbon dioxide that is removed from the atmosphere through the Direct Air Capture process. This project, if constructed, will show that it is possible to create an environmentally friendly chemical plant that can produce important fuels such as methanol while maintaining carbon neutrality.

I. INTRODUCTION

The world is dependent on fossil fuels for energy and manufacturing, resulting in significant greenhouse gas emissions and leading to environmentally damaging outcomes such as global warming. As the world population continues to increase, the negative impacts of fossil fuel use will only compound. As such, work must be done to understand how carbon dioxide concentrations in air can be reduced, and how industrial practices can be changed to achieve sustainability goals.

Direct air capture (DAC) is a new type of technology that was first introduced in the late 20th century, serving to decrease ambient carbon dioxide concentrations. It is seen as a key component to decrease the total concentration of carbon dioxide in the atmosphere (Dent, 2021). While capturing carbon dioxide directly from ambient air presents its challenges compared to traditional carbon capture technologies that operate at large point emission sources, like a fossil-fuel based power plant, direct air capture is still a promising method to capture carbon and allows for net-negative emissions. With goals proposed in the Paris Climate Agreement of limiting warming 2℃ below pre-industrial levels, many believe that the only way of achieving this is to begin creating negative carbon emissions (“Negative emission technologies…”, 2018). Direct air capture has the potential to lower the ambient concentration of carbon dioxide without a large contribution of emissions if used on a large scale; for this reason, direct air capture technology was researched to provide a proof of concept for future development.

Methanol is an example of a versatile but damaging chemical as well as fuel that is widely utilized in the transportation and energy industries as it is a liquid fuel, and therefore has high energy density (Morrison, 1992). Traditionally, methanol is produced via synthesis gas, a gas mixture produced through natural gas reforming and coal combustion. Although this manufacturing process is well-developed, the utilization of fossil fuels generates greenhouse emissions, contributing to the harmful effects of climate change. To this end, the proposed project aims to research and develop a sustainable pathway to produce methanol. Specifically, the project focuses on designing a methanol synthesis process that utilizes carbon from direct air capture and blue hydrogen to create a net carbon-neutral methanol production system. Carbon dioxide will be directly captured from ambient air via a designed direct air capture system and hydrogen will be purchased through a third party to be utilized for the production of methanol.

Hydrogen is a necessary feed for methanol production, and it will be purchased from a third party source. In industry, hydrogen can be classified based on the type of plant it is sourced from. For example, blue hydrogen is produced from natural gas in a plant that has an integrated carbon capture and storage system. As blue hydrogen does not contribute to carbon emission rates, this project seeks to use it as a feedstock. The production of blue hydrogen is outside the scope of this study, but its purchase will be researched through an economic lens.

This overall process is designed to be “carbon-neutral,” meaning that the carbon emitted from the consumption of the produced methanol will be equal to the carbon captured from the direct air capture process.

The novelty of this proposed process is its encapsulation of three different functional components into a singular process: carbon from direct air capture, blue hydrogen, and downstream liquid fuel production.

II. PREVIOUS WORK

2.1. Direct Air Capture Previous Work

Direct air capture is a relatively new technology, with nineteen direct air capture plants operating worldwide today. There is concern about the feasibility of direct air capture due to the complexity and cost of drawing in carbon dioxide from ambient air and processing it which holds back further development. At the moment, the capacity of the plants in operation are 0.01 megatonne-CO_2/ year (Mt-CO_2/year) and a 1 Mt-CO_2/year plant is in advanced development. There are hopes to scale up DAC capture to over 85 Mt-CO_2/year by 2050 in order to reach the "Net Zero Emissions by 2050" scenario (Budinis, 2021).

There are two approaches to achieve capture of ambient carbon dioxide; first, liquid direct air capture allows for the passage of air through solutions which react with the carbon dioxide residing in the air and can then be sent to further processing to produce a pure stream of carbon dioxide. This approach requires high heat and also features chemical regeneration to create a continuous process. The second approach is solid direct air capture; here, solid sorbents in filters bind with carbon dioxide, which can then be heated to release carbon dioxide and be stored or used. This report will focus on the study of liquid direct carbon air capture and will report previous works in this area (Businis, 2021).

2.1.1. Carbon Engineering

Carbon Engineering (CE) is a Canadian based company, founded with the purpose to improve and commercialize direct air carbon capture technology at a "megaton-scale" (Carbon Engineering, 2021). Carbon Engineering has developed a pilot scale plant, with a capacity of approximately one tonne of CO_2 per year (t-CO_2/year). Design of the chemical system and process flow as well as results from the pilot plant, including energy balances, material balances, process flow diagrams, experimentally determined extent of reaction values, fluidization velocities, particle sizes, equipment used, and other relevant information are reported on in their 2018 paper "A Process for Capturing CO_2 from the Atmosphere", written by David Keith, Geoffrey Homles, David St. Angelo, and Kenton Heidel.

Additionally, this report proposes a scale-up of their pilot plant from a capacity of 1 t-CO_2/year to a 0.98 megatonne per year (Mt-CO_2/year) capacity and the associated, detailed cost analysis. The following report uses the Carbon Engineering pilot plant and scale-up as a basis for design and economic analysis. Though, there are many key differences that allow for a novel approach.

2.1.2. Existing Modeling Research

Beyond the pilot plant created by Carbon Engineering, universities have contributed to DAC research by publishing theses detailing the modeling process, specifically through ASPEN software. One university thesis from the Politecnico di Torino entitled "Process modeling of a Direct Air Capture (DAC) system based on the Kraft process," modeled the entire Carbon Engineering process by drawing assumptions from the pilot plant data to decide appropriate ASPEN blocks for each unit operation. The modeling was based on using two thermodynamic models: Electrolyte NRTL (Non-Random Two-Liquid) for liquid phase streams and SRK EoS (Soave-Redlich-Kwong Equation of State) for gas phase streams (Magistrale, 2018). The Electrolyte-NRTL model was used to account for the ionic dissolution occurring between solid components and water streams, and SRK EoS generally is used for gaseous components as it accurately describes relationships between temperature, pressure, and volume of gasses (Magistrale, 2018). The thermodynamic modeling choices from this thesis were accepted in this design report; however, this design report varies in Aspen Plus block choices for major unit operations (i.e. Pellet Reactor and Calciner).

2.2. Methanol Synthesis Previous Work

2.2.1 CAMERE Process

Unlike the novelty of Direct Air Capture, methanol production has been well established in industry as methanol has a multitude of uses across many different fields of work. The industry standard for methanol production is to take the synthesis gas, produced from petroleum sources or natural gas, and hydrogenate it to produce methanol (María et al., 2013). The feedstock of syngas already contains the necessary CO and H_2 from the oil and gas source, and thus it is much simpler to just run the syngas through a reactor with the proper catalysts to produce methanol at an efficient and profitable rate. The main difference between the design that will be used in this project compared to the industry standard of methanol production is the feed syngas. We do not have a source that can provide CO and H_2 in one stream, so H_2 must be outsourced and brought into the plant site, while CO will be obtained from the captured CO_2 in the Direct Air Capture unit.

Our process was based on the CAMERE process, developed by Oh-Shim Joo et al. The CAMERE process directly uses carbon dioxide and produces carbon monoxide gas via the reverse water gas shift reaction, just like traditional industry methods. However, the source of this carbon dioxide gas is not from petroleum products like other industry standard methanol production feeds are. Because of this, hydrogen gas is also needed as a feed. The lack of dependence on petroleum products is what made this designed process favorable for the basis of this report's methanol production design. This project took assumptions about the overall conversion and rates of reactions from the previously mentioned study to model the larger scale production proposed. The CAMERE Process was performed in a mini pilot setting in a laboratory.

III. DISCUSSION

3. Overall Design Basis

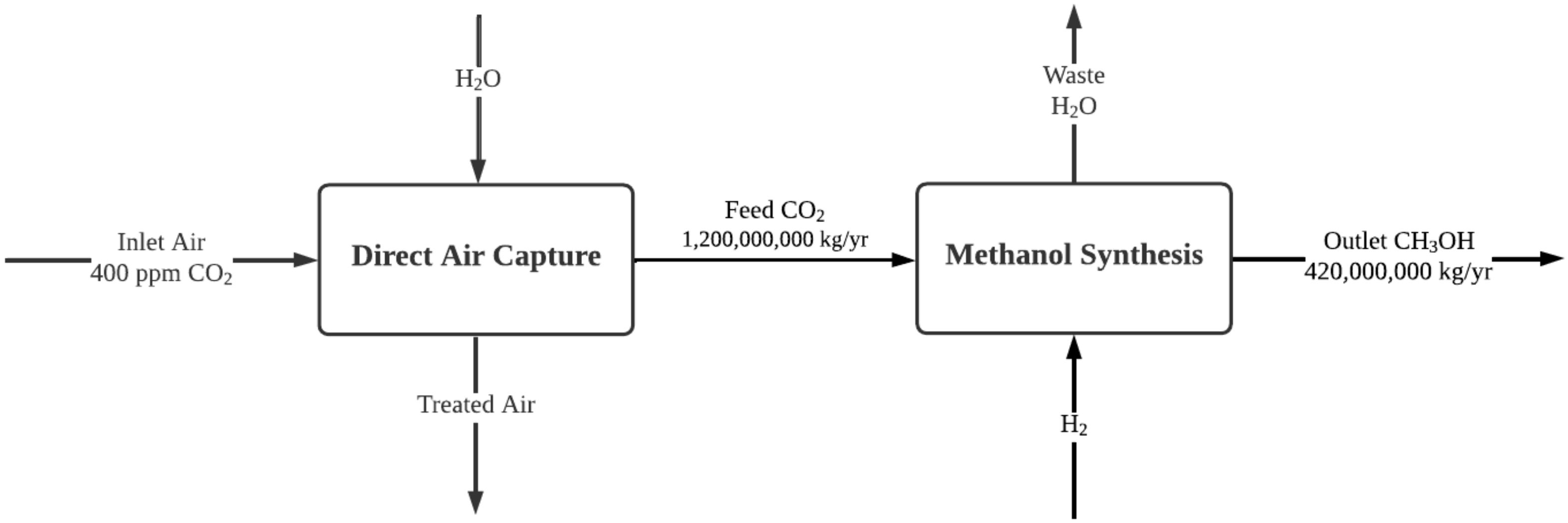


Figure 3-1 DAC and Methanol Production Block Flow Diagram

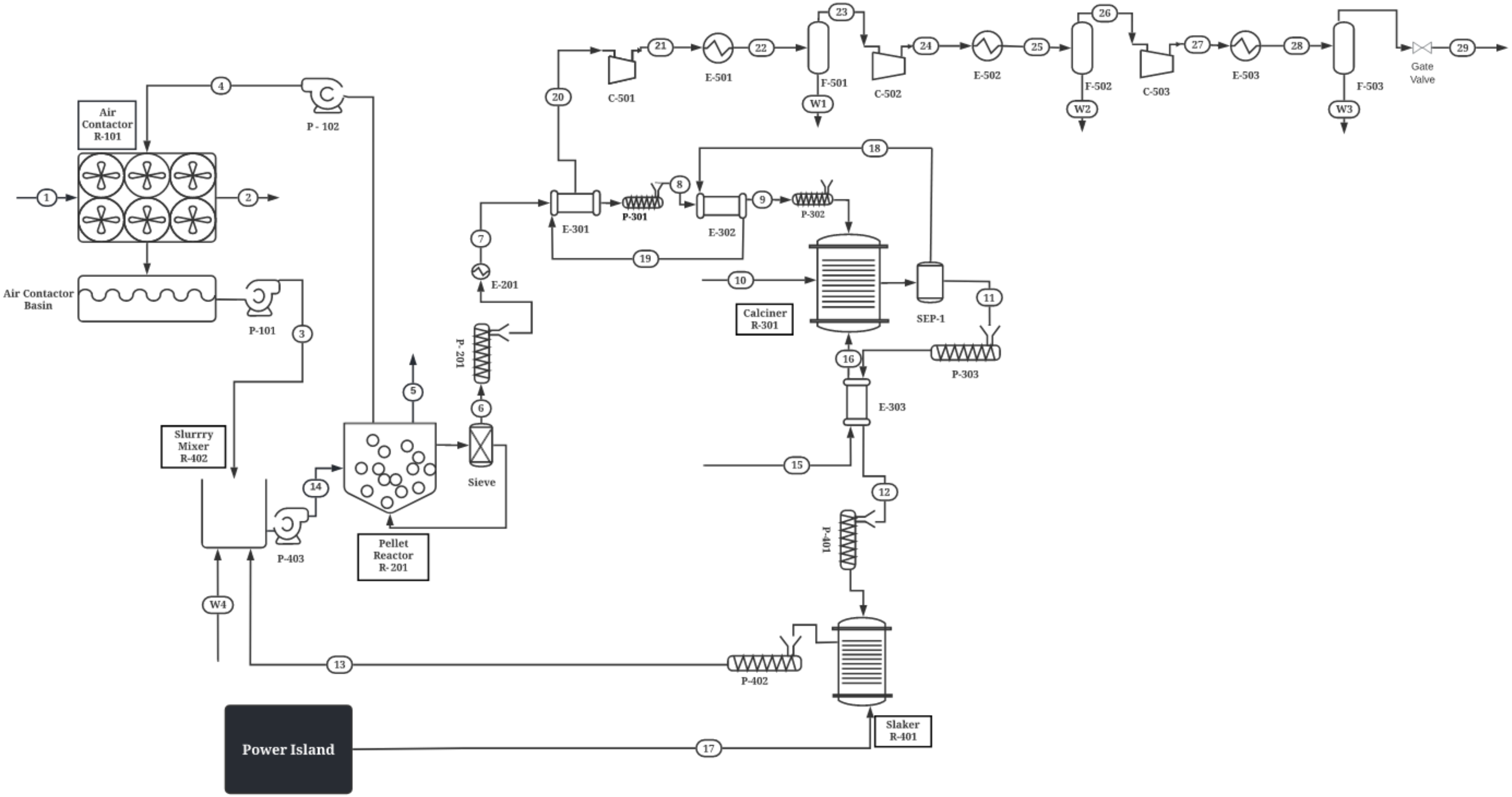


Figure 3-2 DAC Process Flow Diagram

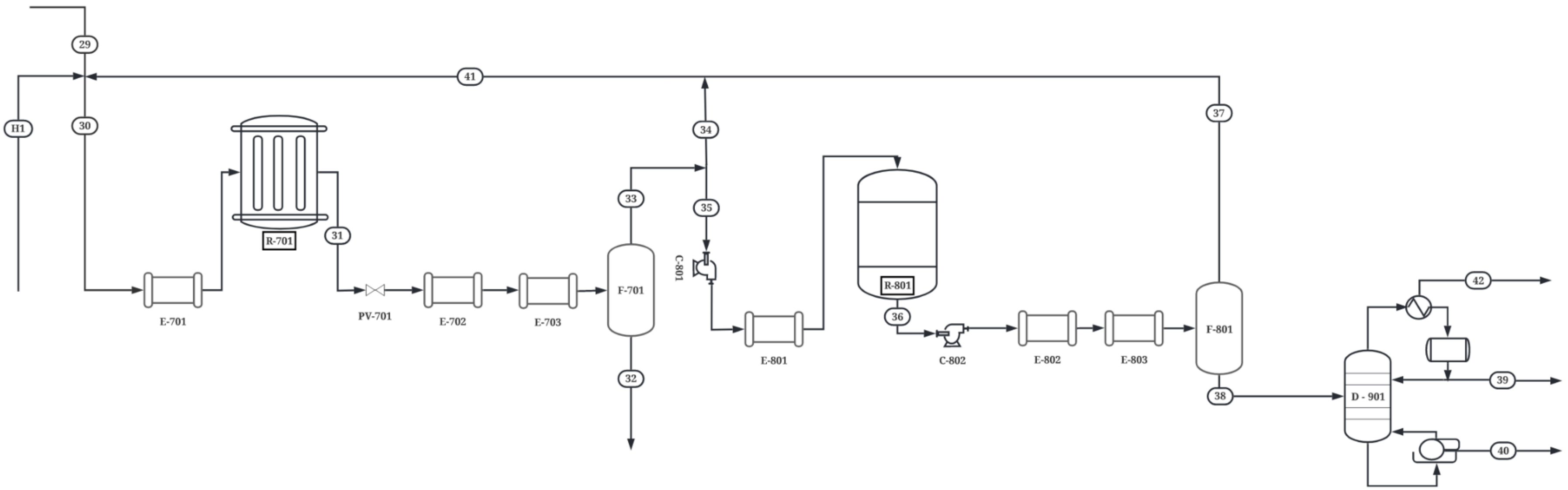


Figure 3-3 Methanol Synthesis Process Flow Diagram

3.1.1. Direct Air Capture Design Basis

The first objective of this project is to produce carbon dioxide (CO_2) via a designed Direct Air Capture (DAC) system. This purified carbon dioxide stream will later be used as a feed in methanol synthesis.

From initial research on current and available technology, there are two main options for DAC technology: high-temperature aqueous solutions (HT DAC) and low-temperature solid sorbent (LT DAC) systems. Through literature review, it was found that the HT DAC system is the most robust and developed of the two options. While LT DAC has the benefit of requiring lower temperature inputs, HT DAC improves upon LT DAC as the capacity is higher and it is a continuous process (Broehm, 2015). Capacity, as well as maintaining continuous production, are decided to be more important than potential energy savings in the consideration of scale-up. For these reasons, HT DAC was used in this design process. There are also options for different high-temperature aqueous solution sorbent types. In this design, a potassium hydroxide sorbent was chosen for the capture solution for the air contactor. Other hydroxides, like sodium hydroxide, were considered but rejected as the KOH sorbent produced high purity streams of carbon dioxide (Fasihi et al, 2018).

In the chosen high-temperature aqueous solution based DAC, a potassium hydroxide sorbent connected to a calcium caustic loop is used to recover carbon dioxide, see **Figure 3.1.1-1** (Keith et al., 2018). This is accomplished through the use of four major unit operations: air contactor, the pellet reactor, the slaker, and the calciner, as seen in **Figure 3.1.1-1**.

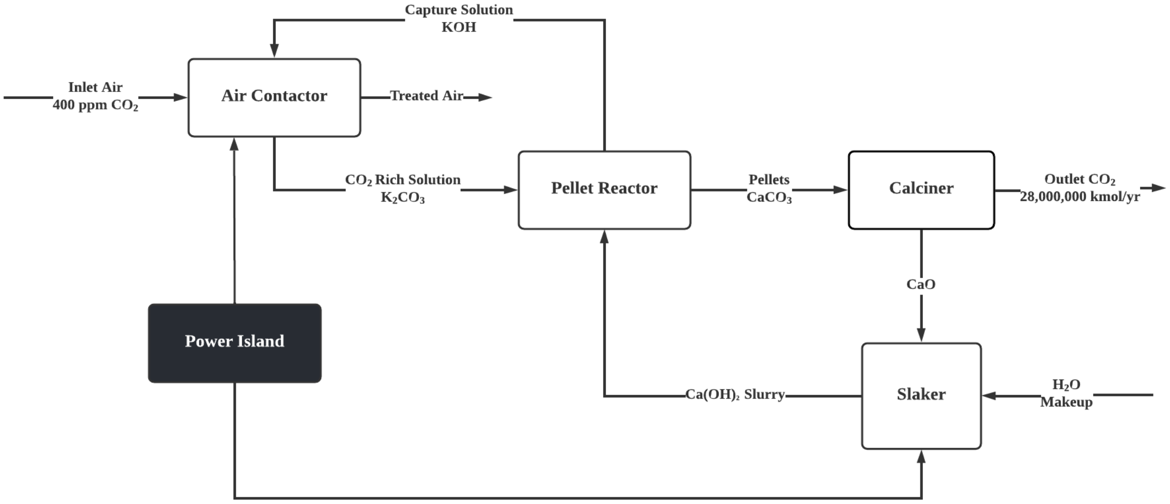


Figure 3.1.1-1 Simplified High-Temperature Aqueous Solution Direct Air Capture Process

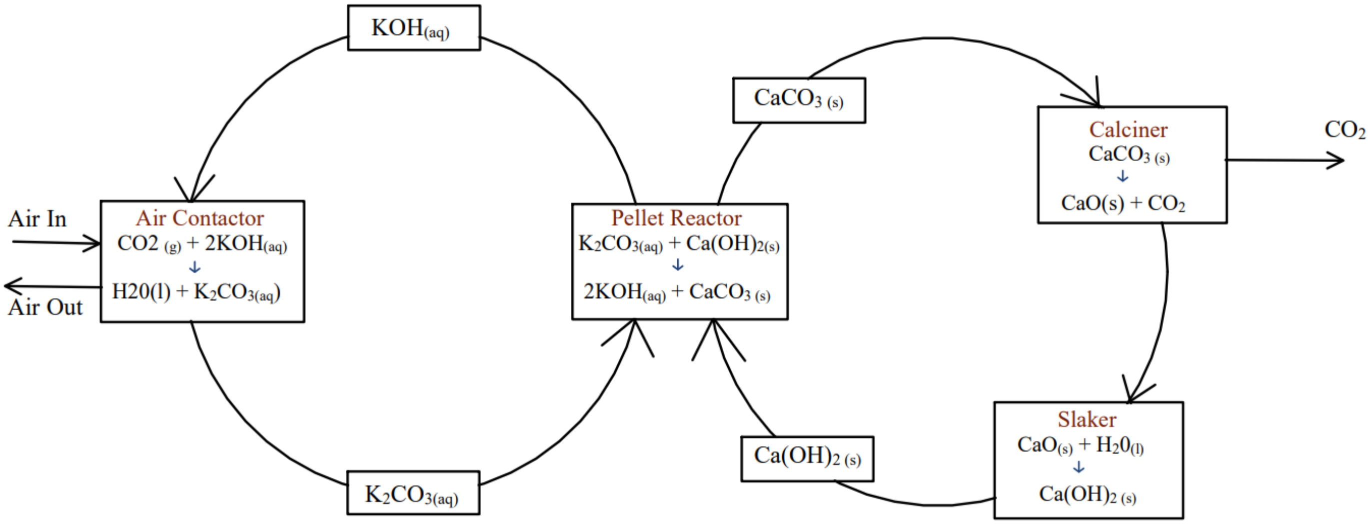


Figure 3.1.1-2 CO_2 Production Via Potassium Hydroxide Sorbent and Calcium Caustic Recovery Loop System (Keith et al., 2018)

The objective of the first unit operation, the air contactor, is to draw in the primary feed stream for this process, ambient air. Air is drawn in through large fans connected to the air contactor and the carbon dioxide present in the ambient air is allowed to react with an aqueous sorbent in the system. The average of carbon dioxide concentration in the United States is between 400 and 420ppm; therefore, for the purposes of this study a carbon dioxide concentration of 400 ppm in air is assumed (OEHHA, n.d.). Table 1 illustrates the molar composition of the assumed ambient air drawn which acts as the main feed for this process.

Table 3.1.1-1 Direct Air Capture Inlet Compositions

Component	**Ambient Air Molar Composition**
Carbon Dioxide	0.000391
Oxygen	0.206
Nitrogen	0.778
Water	0.0156

In the air contactor, gas absorption takes place in a cross-flow cooling tower, as proposed by a DAC pilot plant by Carbon Engineering (Keith et al., 2018). The air contactor consists of a vertical tower made of plastic packing with the alkaline solution flowing down the structure. As described in the pilot plant report, flows of the aqueous solution are adjusted in order to avoid issues related to build up from particulates in the air. After air is drawn into the contactor and passed over a thin film of potassium hydroxide (KOH) solution, ambient carbon dioxide binds to the sorbent and forms potassium carbonate (K_2CO_3). The necessary solution used in the air contactor for an initial reaction to take place will be an aqueous solution of 1.0M OH^-, 0.5M CO_3^{2-}, and 2.0M K^+. The air contactor operates at 21℃ and ambient pressure.

Multiple hydroxide-based compounds can be used for the correct reactions to take place, but as mentioned previously potassium hydroxide is cost-competitive with other options, and has reliably high purity (Keith et al., 2018). The formula for the reaction is as follows:

$$\text{(Eq. 1) } 2KOH_{(aq)} + CO_{2\,(g)} \rightarrow H_2O_{(l)} + K_2CO_{3\,(aq)}$$

Next, the pellet reactor separates the salt produced from the carbon dioxide-rich solution leaving the air contactor, creating pellets.. The reaction will take place in a fluidized bed reactor where a slurry of $Ca(OH)_2$ is injected into the bottom of the reaction vessel, and pellets of $CaCO_3$ are then formed as $Ca(OH)_2$ dissociates into Ca^{2+} and subsequently reacts with CO_3^{2-}. The formula for the reaction is as follows:

$$\text{(Eq. 2) } K_2CO_{3\,(aq)} + Ca(OH)_{2\,(s)} \rightarrow CaCO_{3(s)} + 2KOH_{(aq)}$$

These pellets are then sent to the Calciner in which they are mechanically agitated and heated to high temperatures to produce CO_2 gas and solid calcium oxide pellets. The reaction is as follows:

$$\text{(Eq. 3) } CaCO_{3\,(s)} \rightarrow CaO_{(s)} + CO_{2\,(g)}$$

The calciner is designed to be an adiabatic direct oxy-fired rotary calciner reactor that continuously injects pre-heated oxygen and methane directly with the calcium carbonate pellets. The combustion reaction between oxygen and methane, as shown below, provides enough heat for the pellets' temperature to increase from 300℃ to 900℃ as the reaction is exothermic.

$$\text{(Eq. 4) } CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{(g)}$$

This reaction also produces carbon dioxide which increases the overall yield. At this point, the initial product carbon dioxide stream is sent to a series of compressors and water is removed to produce a final, purified carbon dioxide stream with a **purity of at least 99.8%.** This stream is then ready to be utilized for the production of methanol.

To regenerate the capture solution for further extraction of carbon dioxide from the air, the calcium oxide travels to the next unit operation, the slaker. Here, steam is added to the reactor along with calcium oxide from the calciner in order to precipitate calcium hydroxide to be reused in the process. This takes place at 300℃ and ambient pressure. The formula for the reaction is shown below:

$$(\text{Eq. 5})\ CaO_{(s)} + H_2O_{(g)} \rightarrow Ca(OH)_{2\,(s)}$$

Material balances were conducted based on reported extents of reaction and values are reported in the stream table below, see **Table 3.2.9-1.**

Thus far, only one company has implemented wide-scale HT DAC (Fasihi, 2019), so there is ample opportunity for competitors to develop their own versions. This proposed project provides an avenue for improvement with the addition of downstream processing of CO_2. Therefore, providing a novel way to improve the economics and utility of DAC as traditional DAC design usually sequesters carbon in geological formations, or the carbon is used in enhanced oil recovery.

3.1.2. Methanol Synthesis Design Basis

The carbon dioxide yielded from the DAC system described above is then utilized to produce methanol. In a set of multiple reactors and separators, a product stream of **methanol (CH_3OH) at a purity of 99.6%** is produced. In order to run this process, a few key materials are needed for the methanol synthesis, the carbon dioxide produced from the DAC system as well as purchased blue hydrogen. Additional catalysts are needed in order to promote the proper reaction in each of the reactors, which will be discussed in detail as a part of the process description.

Production of methanol via carbon dioxide from DAC and blue hydrogen occurs through two chemical reactions, known as the CAMERE Process. The first reaction is the reverse water-gas shift reaction that converts carbon dioxide (CO_2) to carbon monoxide (CO); this is followed by the second reaction, the hydrogenation of CO. These two reaction pathways are summarized below in (Eq. 6) and (Eq. 7) respectively:

$$(\text{Eq. 6})\ CO_2 + H_2 \Leftrightarrow CO + H_2O$$

$$(\text{Eq. 7})\ CO + 2H_2 \Rightarrow CH_3OH$$

To achieve the desired reactions, streams of carbon dioxide and hydrogen gas are fed into the first unit operation used in this system, where the reverse-water gas shift reaction takes place. Based on literature, the conditions for this reactor are determined to be 500ºC and 10.1 bar. The product stream from this reactor is then sent to a condenser for the removal of excess water. The resulting gas mixture is then compressed and fed into a subsequent reactor, the Methanol Synthesis Reactor where the hydrogenation of carbon monoxide takes place. As seen in **Figure 3.1.2-1,** the product stream from the Methanol Synthesis Reactor is then sent through two separation units, a condenser and distillation column, to acquire a final, purified stream of methanol. The conditions for the Methanol Synthesis reactor are 250ºC and 30.4 bar (Joo, 1999).

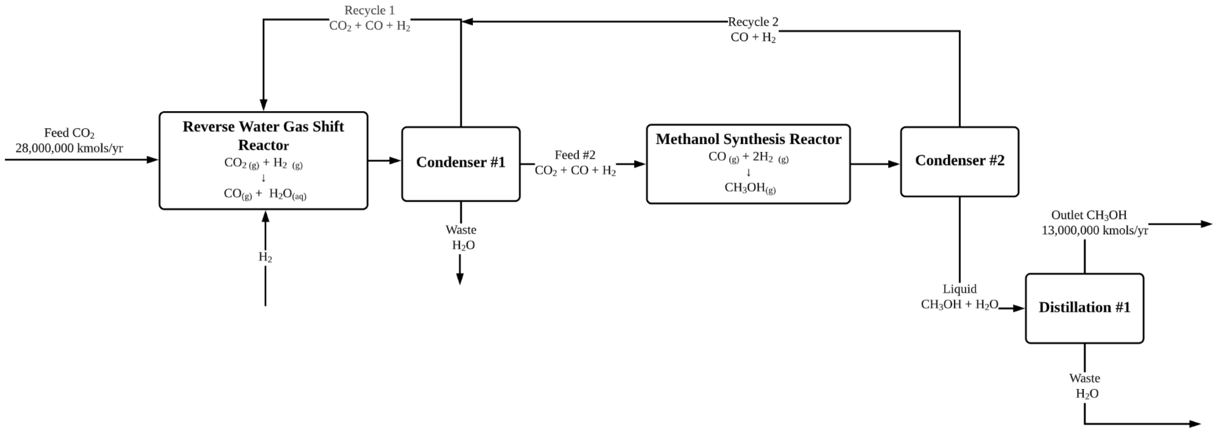


Figure 3.1.2-1 Methanol Block Flow Diagram

The first condenser unit is designed to remove the majority of the water produced in the Reverse Water Gas Shift Reactor. The remaining gasses are partially recycled back into the Reverse Water Gas Shift reactor while the rest is sent to a compressor before the Methanol Synthesis reactor. The second condenser unit is designed to condense the methanol and any remaining water from the reactor effluent stream. Finally, the methanol and water stream is sent to a distillation column while the remaining gasses are recycled back to the Reverse Water Gas Shift reactor. The final methanol product stream leaves from the aforementioned distillation column.

Both reactors require catalysts for the desired reaction pathways to occur. From literature, it was determined that the best catalyst to use in the Reverse Water Gas Shift reactor is ZnO/Al_2O_3 (1:2) (Joo, 2003). The purpose of this catalyst is to promote the conversion of CO_2 to CO and this will in turn maximize methanol production (Joo, 2003).

Additional literature review showed that there are a few options for the catalyst used in the Methanol Synthesis Reactor to promote methanol yield. One particular catalyst, $Cu/ZnO/ZrO_2/Ga_2O_3$ (5:3:1:1), allows for higher methanol yield per pass and maintains better stability and reactivity. The second option for this reactor's catalyst is $Cu/ZnO/Al_2O_3$. This catalyst is the current industry standard and is able to have an adequate selection for methanol (Joo, 1999).

A material balance was done using the carbon dioxide yield from the DAC material balance and literature conversions of reactions. Similar to the first material balance, multiple assumptions were made for this material balance, see **Table 3.3.5-1.**

This process aims to extract 1 billion kilograms of carbon dioxide from the atmosphere per year and produce a purified product stream of carbon dioxide to then be sent downstream to be processed into methanol. The goal of the methanol synthesis is to yield 412 million kilograms of methanol per year at a production schedule of 6000 hours per year, which is about 7% of the annual production of methanol in the United States. The scale of this project was based on a published report by Carbon Engineering where a direct air capture plant was designed with a capacity to produce 0.98Mt of carbon dioxide per year based off of an internal pilot plant. From this, a balance was done to understand the resulting methanol yield that could be possible at this production rate.

3.2. Direct Air Capture Design

As seen in **Figures 3-1 and 3-2**, the DAC to methanol synthesis production process is large and complex. Therefore, this report will first discuss the DAC process block-by-block, then discuss the methanol synthesis process block-by-block. See **Figure 3-2** for overall view of the DAC process.

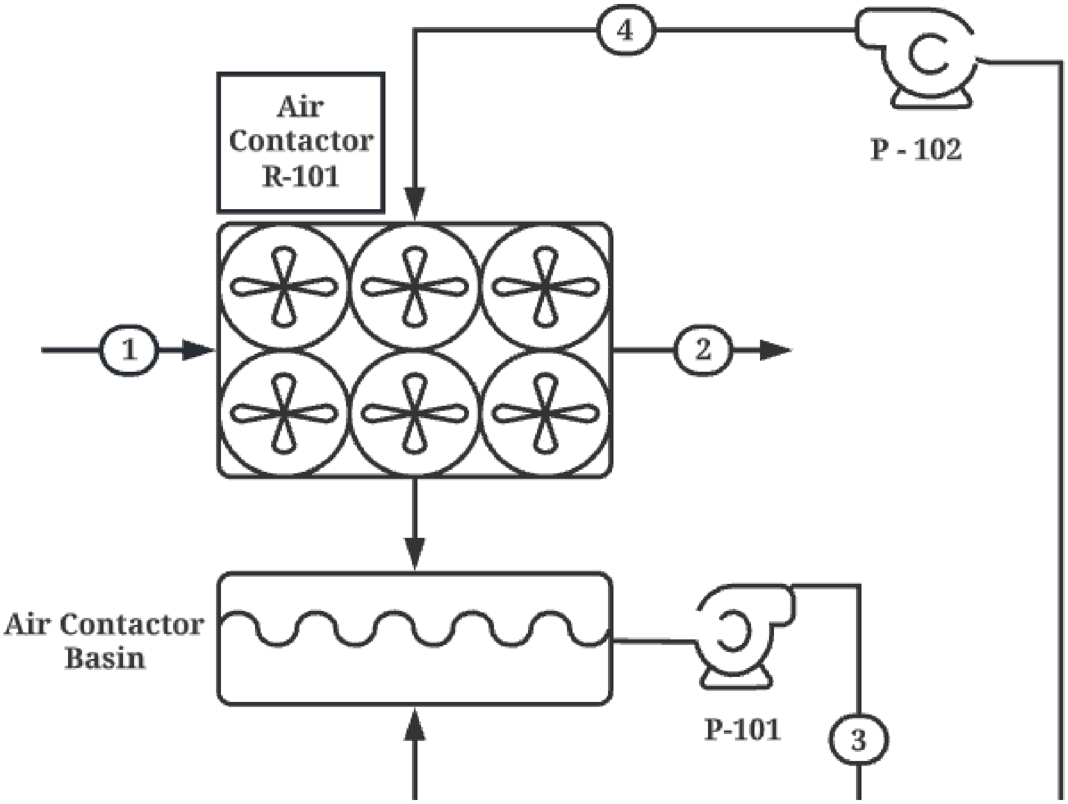


Figure 3.2.1-1 Block 1

The first block, see **Figure 3.2.1-1,** in the system contains the main air contactor reactor as well as two pumps to transport the product stream to the next unit, the K_2CO_3 rich stream, and to transport regenerated solvent from Block 2 back to Block 1, the KOH rich stream.

Air Contactor Reactor

The purpose of the air contactor is to draw in ambient air via large fans and contact it with an aqueous potassium hydroxide (KOH) sorbent. Here, the carbon dioxide residing in the air reacts with potassium hydroxide to form potassium carbonate (K_2CO_3). Potassium carbonate is then sent to the pellet reactor to react with calcium hydroxide to form calcium carbonate pellets, which is decomposed to form a purified stream of carbon dioxide. The primary reaction occurring in the air contactor is as follows:

$$\text{(Eq. 8)}\ \ CO_{2\,(g)} + 2KOH_{(aq)} \rightarrow\ H2O_{(l)} +\ \ K_2CO_{3\,(aq)}\ \ \Delta H° = -95.8\ \text{kJ mol}^{-1}$$

Unit Design: The air contactor is a unit designed by Carbon Engineering and based on forced-draught cooling tower technology. In this unit, large fans draw in air which is then introduced to a thin film of potassium hydroxide at 1 Bar and 21℃. The potassium hydroxide solution flows downward on the surface of a structured plastic packing and would interact with air in a cross-flow configuration (Keith et al., 2018). Due to the proprietary design, and complexity of mass transfer between the air and the aqueous solution, this unit is blackboxed for this project. Though, work was completed to gain a general understanding of the conversion from carbon dioxide to potassium carbonate at equilibrium.

Energy Analysis: The primary chemical reaction occurring in the air contactor is exothermic, however, simulations show that the outlet stream decreases by approximately 3℃. While it is unexpected that this stream would decrease in temperature due to the exothermic nature, this can be explained by the evaporation of water occurring in the air contactor which is not present in the chemistry from Equation 8.Within the air contactor, a large amount of water that evaporates as the aqueous solution comes in contact with the inlet air and leaves the system through the treated air, stream 2. It is likely this evaporative, endothermic behavior removes more heat than supplied by the reaction in Equation 1. Energy considerations are assumed to be negligible and this unit will likely be run adiabatically.

Material Balance: While the Carbon Engineering reference pilot plant has a published carbon dioxide absorption rate of 74.5%, the material balance for the air contactor was conducted based upon Aspen Plus simulation results, generating data that represents the best-case capturing scenario thermodynamically. Aspen Plus simulations produced a 99.90% absorbency, which is likely higher than actual absorbency. However, the rate of drawn in air can be increased to account for discrepancies in mass balances between simulations and real behavior.

Modeling Via Aspen Plus: A simplified air contactor was designed in Aspen Plus, utilizing the electrolyte package with the ENRTL-RK base method. This strategy allows for the simulation to model the dissociation of compounds into their ions in solution, which is needed in the reaction between carbon dioxide and aqueous hydroxide sorbent used for this process, potassium hydroxide. The process was modeled with a Flash2 unit to understand possible absorption at equilibrium, and the results showed 99.90% of carbon dioxide in air reacts with potassium hydroxide. A Flash2 unit was used as the electrolyte package required a flash process to model dissociation of compounds. See **Figure 3.2.1-2** for the Aspen Plus configuration and **Table 3.2.1-1** for relevant simulation details. Results of the stream content are reported in the stream tables, see **Table 3.2.9-1.**

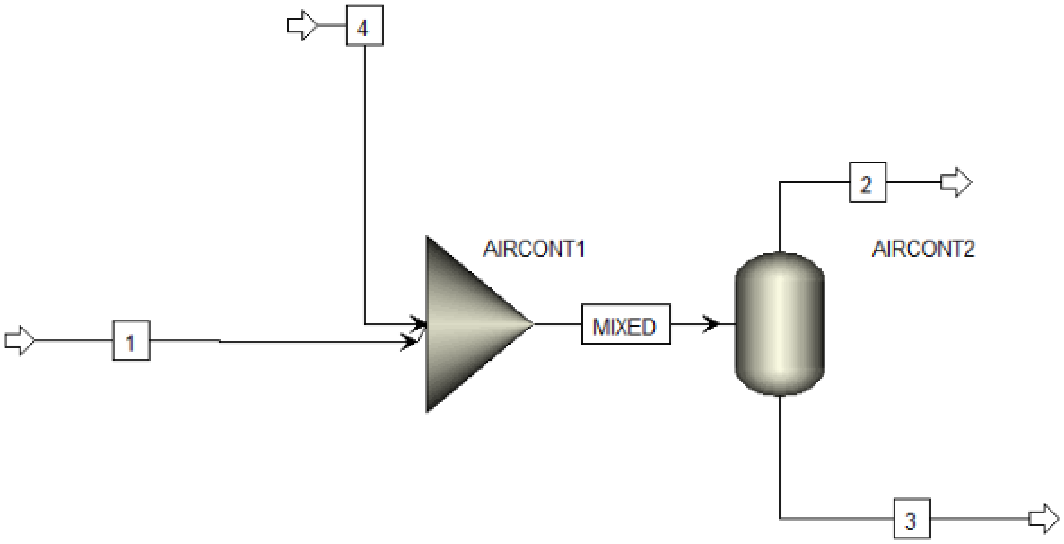


Figure 3.2.1-2 ASPEN Air Contactor Reactor Model

Table 3.2.1-1 Air Contactor ASPEN Details

Block	Type	Temp (C)	Pressure (Bar)	Heat Duty (MW)
AIRCONT1	Mixer	undefined	1	0
AIRCONT2	Flash2	undefined	1	undefined

3.2.2. Block 2: Pellet Reactor

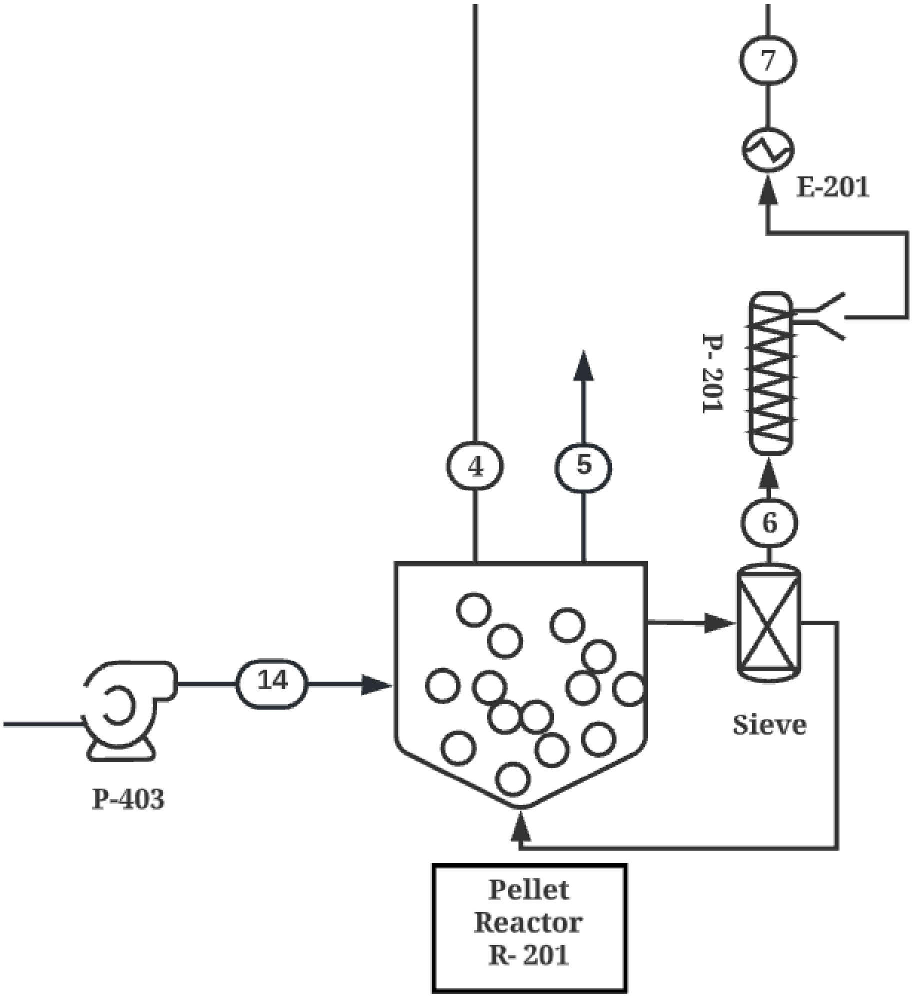


Figure 3.2.2-1 Block 2

Block 2 consists of the main pellet reactor unit as well as a heater and a conveyor. Of note, the depicted sieve and recycle stream is included to illustrate the type of reactor used, and this behavior is integrated into the system. Therefore, it is not designed. Additionally, all heat exchanger designs will be described in section **3.2.7.**

Pellet Reactor

The purpose of the pellet reactor is to form calcium carbonate pellets via a salt metathesis reaction between potassium carbonate formed in the air contactor and calcium hydroxide formed in the slaker. Calcium carbonate is the product of interest in this unit and will be sent to the calciner to be decomposed into the target product of the direct air capture process, carbon dioxide. The reaction proceeds as follows:

(Eq. 9) $K_2CO_{3\,(aq)} + Ca(OH)_{2\,(s)} \rightarrow 2KOH_{(aq)} + CaCO_{3\,(s)}$ $\Delta H° = -5.8$ kJ/mol

Unit Design: The pellet reactor is designed to be an adiabatic fluidized bed crystallizer, operating at 1 Bar and 25℃. A fluidized bed reactor was chosen as it allows the incoming aqueous potassium carbonate to interact with calcium hydroxide, and for subsequently precipitated calcium carbonate to interact with calcium carbonate seed pellets suspended in the system. Calcium carbonate pellets develop and accumulate mass in this reactor until they reach a certain size, in this case >0.85mm, before they are sent downstream to the next process to be decomposed into carbon dioxide (Keith et al., 2018). The size of the pellets was chosen to be the same as used in the Carbon Engineering pilot plant.

Energy Analysis: This is a slightly exothermic reaction and was found to form enough energy to increase the outlet stream by <3℃ via Aspen Plus simulations, therefore this reactor is designed to be adiabatic and no heat is added or removed. Energy considerations are considered to be negligible as temperature changes at this level are inconsequential to the process.

Material Balances: To determine mass balances, the "calcium retention" rate reported by Carbon Engineering was assumed to be equivalent to the extent of reaction over the pellet reactor system as it is said to be a measurement of pelletization performance (Keith et al., 2018). Calcium retention, which was determined experimentally at the reference pilot plant, is loosely defined as the ratio of total added calcium retained on the pellet as a fraction of active calcium fed to the system (Burhenne, 2017). Refer to **Table 3.2.9-1**for material balance.

Reactor Dimensions Calculations: In addition to operating conditions and energy requirements, the dimensions of the pellet reactor were also investigated. To determine reactor dimensions, the kinetics modeling is typically used to understand residence time. However, in the case of the pellet reactor, knowledge of the growth kinetics of calcium carbonate ($CaCO_3$) pellets is necessary to estimate a residence time for the product stream as pellets will only be sent downstream once size specification is reached. For reference, a reasonable pellet size is >0.85mm, therefore growth models will evaluate a change in pellet size from 0.1mm to 0.85mm, representative of typical seed pellet size to the final pellet size. The size of the pellets remaining in the system is controlled by a sieve inside the reactor that allows retention of pellets that have not developed enough.

To determine the dimensions of the pellet reactor, it is necessary to understand the growth rate of calcium carbonate pellets at the operating conditions of the reactor. The growth rate of calcium carbonate is dependent on the superficial velocity of the fluids, supersaturation of calcium carbonate, and initial pellet size of the seed. Based on literature, the growth rate equation of calcium carbonate in a pellet fluidized bed reactor can be modeled as Equation 10 below (Hu, 2017).

(Eq. 10) $$G = K_g * SV^a * L_0^b * S^c$$

where K_g is the coefficient of linear growth rate, SV is the superficial velocity (m/h), L_0 is seed pellet size (mm), and S is supersaturation (kg solute/kg water)

Using calcium carbonate growth rate data extracted from research done by Hu et al., a least squares method via computational software, Matlab, was employed to determine the coefficient of linear growth rate (K_g) and the exponents (a,b,c) for each parameter. The modeled rate expression based on the experimental data is shown in Equation 11.

$$\text{(Eq. 11)} \quad G = 1.0064 * 10^{-18} * SV^{2.818} * L_0^{-0.6556} * S^{1.9353} \quad \text{[m/s]}$$

The operating conditions of the pellet reactor were chosen to be a superficial velocity of 300 m/hr, initial pellet size of 0.1 mm, and a supersaturation of 84.4 kg solute/kg water. The initial pellet size and supersaturation chosen imitate the operating conditions from the experimental data (Hu, 2017). The superficial velocity of 300 m/hr was chosen to yield a reactor with a growth rate comparable to published rates and a reasonable volume. With these parameters, the growth rate was modeled to be $2.33 \cdot 10^{-7}$ m/s. From this information, the residence time of the reactor could be determined based on Equation 12, assuming the mean crystal size to be the size of the pellets leaving the pellet reactor, 0.85 mm (Kramer, 2019).

$$\text{(Eq. 12)} \qquad L_m = \frac{G*\tau}{4}$$

where L_m is the mean crystal size (m), G is the growth rate (m/s), and τ is the residence time of the reactor (s)

Based on this calculation, the residence time was found to be 0.48 hours or roughly 29 minutes. With this, the volume of the reactor was calculated to be 66 m^3. Using an industry standard height to diameter ratio, R_{HD}, of 2 and Equation 13, the diameter of the pellet reactor can be determined (Kramer, 2019).

$$\text{(Eq. 13)} \qquad D = \sqrt[3]{\frac{4V}{\pi}}$$

Where *V* is volume (m^3) and *D* is pellet diameter (m)

The diameter and height of the reactor were calculated to be 3.48 m and 6.95 m, respectively. However, for ease of purchasing, the diameter and height of the reactor were rounded to be 4 m and 7 m, respectively, with a higher volume of 87.7 m^3.

Another essential design aspect of the pellet reactor is management of the calcium carbonate fines. Fines are defined as small masses of calcium carbonate formed in localized areas of supersaturation that exit the reactor failing the size specification of 0.85 mm. These fines will be filtered out using a sieve to be processed and to control the size specification of the outlet stream. Calcium carbonate seed will also be needed within the system to proliferate the formation of calcium carbonate pellets. This will be achieved by recycling unreacted calcium carbonate from the calciner.

Modeling Via Aspen Plus: The pellet reactor was designed using the Aspen Plus electrolyte package with ENTRL-RK base method to account for the dissociation and precipitation reactions necessary in the unit operation (“Aspen Physical Property System,” 2001). The electrolyte package accounts for the ionic interactions which is essential for the salt metathesis reaction taking place in the pellet reactor. Initially, the pellet reactor was designed in Aspen Plus as a Mixed Suspension Mixed Product Removal (MSMPR) Crystallizer with the chemistry saturation calculation method and operating conditions of 1 bar and 25℃ as this resembled Carbon Enigneering's design the closest. The issue with this model was that the salt metathesis reaction did not take place and calcium carbonate was not forming. This model was not sufficient, so a Flash2 model with feed streams of pure calcium hydroxide and aqueous potassium carbonate (2.0 M K^+) was implemented instead. This model failed in the same mode as the MSMPR crystallizer model, so it was rejected. A final model was accepted which used an upstream mixer for feed streams of pure calcium hydroxide and aqueous potassium carbonate (2.0 M K^+) and a Flash2 block to separate the products. The inlet and outlet streams for the pellet reactor given by Aspen Plus are shown in **Table 3.2.9-1**. The Aspen Plus configuration of the pellet reactor can be seen in **Figure 3.2.2-2** and notable parameters can be found in **Table 3.3.2-2.**

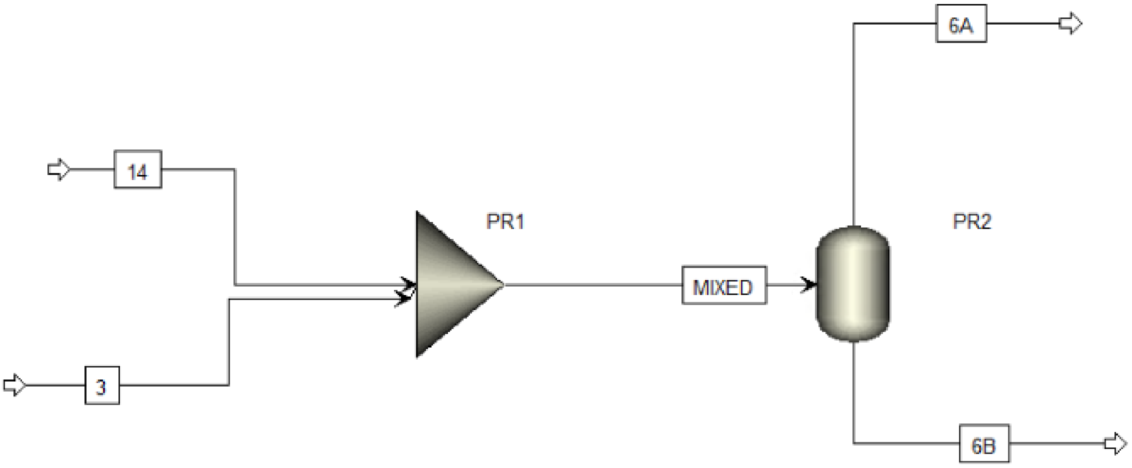


Figure 3.2.2-2 Pellet Reactor ASPEN Model

Table 3.2.2-1 Pellet Reactor ASPEN Details

Block	**Type**	**Temp (C)**	**Pressure (Bar)**	**Heat Duty (MW)**
PR1	Mixer	-	-	-
PR2	Flash2	-	1	0

3.2.3. Block 3: Calciner

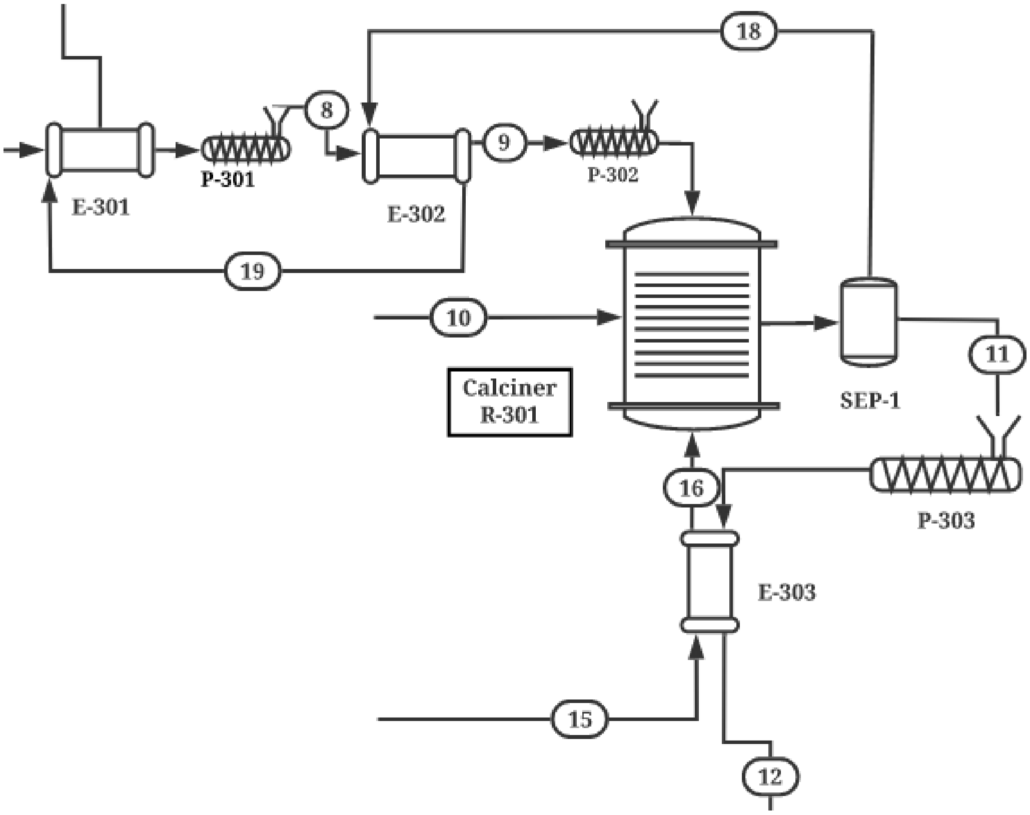


Figure 3.2.3-1 Block 3

Block 3 consists of the main calciner reactors, three solid conveyors, and three heat exchangers. Of note, all heat exchangers are further described in the heat exchanger sections. Additionally, the separator attached to the calciner serves as a representation of what is happening internal to the unit, in that solids and the gasses will flow out of different areas in the system.

Calciner

The purpose of the calciner is to facilitate the decomposition of calcium carbonate pellets formed in the pellet reactor. This reaction produces calcium oxide as well as the target product of DAC, purified carbon dioxide. The primary chemical reaction is as follows:

$$\text{(Eq. 14)} \qquad CaCO_{3\,(s)} \rightarrow CaO_{(s)} + CO_{2\,(g)} \quad \Delta H^\circ = +177.8\ \text{kJ/mol}$$

Due to the endothermic nature of the primary reaction in the calciner, calcium carbonate pellets are continuously heated to 900℃ at ambient pressure (1 Bar). These conditions were chosen as literature shows that calcium carbonate decomposition reactions typically occur between 820℃ and 910℃, with a typical operation temperature being 900℃ (Fedunik-Hofman, 2019).

Unit Design: The calciner is designed to be an adiabatic direct oxy-fired rotary calciner. This reactor will be adiabatic as heat should be retained within the system to drive the dissociation of calcium carbonate, and because high temperatures are needed and these conditions should remain controlled in the unit. Calciners are commonly used to decompose calcium carbonate, specifically in the cement industry. These units can be designed as furnaces, fluidized bed reactors, or rotary kilns. Calciners provide a unit for the reaction to take place, achieving decomposition via high-temperature conditions and agitation via an internal rotating cylinder. A direct-fired rotary kiln calciner is chosen over alternative calciners as it is common in industry and the unit fits within the scope of the project well. Additionally, the direct-fueled unit results in combustion of oxygen and fuel within the system; this highly exothermic process supplies heat and achieves the high temperature of the reactor while maintaining product carbon dioxide in the system, avoiding emissions associated with indirect-fired calciners.

Energy Analysis: While heat is supplied via an in-system combustion, the energy requirements of this endothermic reaction can be evaluated by the equivalent heat duty found via Aspen Plus modeling. This equivalent heat duty was found to be 225MW. Though, economic evaluations are done via the analysis of methane and oxygen purchase costs.

Material Balances: To determine material balances on the system, the extent of reaction reported by Carbon Engineering's DAC pilot plant is used as their study determined the extent of reaction from experimentation and real-world data (Keith et al., 2018). This was done as there are limitations to this calcination process when it comes to evaluating the kinetics, which will be described in subsequent paragraphs.

Reactions of solids are heavily ruled by mass-transfer resistances and thermal conditions. Due to the nature of solid reactors, analysis and reactor design are typically achieved via empirical models that are able to fit the kinetics of decomposition. (Perry, 2008). However, the kinetics of the decomposition of calcium carbonate are widely disputed in terms of how the mechanism is governed and the important kinetic parameters. Some reports indicate that the calcination reaction is controlled by a chemical reaction at the interface, while others suggest that mass-transfer resistance is a more consequential factor (Martínez, 2012). Due to lack of consensus on the reaction order and kinetic constants and that kinetic-based design of calciners are not well researched, this team concludes that kinetics cannot be used to provide a reasonable estimation of reactor size. Therefore, this report can only provide information on the material and energy balance. The capital cost will be found via published correlations on rotary kilns and calculated mass flowrates and temperature requirements as simulated in Aspen Plus in place of providing sizing data. Refer to **Table 3.2.9-1** for material balance.

Modeling Via Aspen Plus: As previously discussed, the calciner unit will be modeled based on an adiabatic direct oxy-fired rotary calciner with a desired operating temperature and pressure of 900℃ and 1 Bar, respectively. As the calciner achieves its extreme temperatures via combustion of injected fuel and oxygen, the feed streams to the calciner include calcium carbonate ($CaCO_3$) from the pellet reactor, oxygen, and methane.

The calcium carbonate inlet flowrate was calculated based on the desired carbon dioxide production, assuming a 98% conversion rate as reported by Keith et al. This flow was modeled to be 650°C based on conditions in literature (Keith et al.), and will be achieved via heat exchangers discussed in a later section. The inlet flowrates for methane and oxygen were determined through the modeling of the calciner to have an outlet stream temperature of approximately 900℃, given that the combustion reaction provides heat. Similarly to the calcium carbonate stream, the oxygen will be injected at a higher temperature achieved via heat exchangers discussed in later sections. It is assumed that the methane stream will be at an ambient temperature of 21℃. Based on the derived Aspen Plus model, 996.6 kmol per hour of methane and 1993.2 kmol per hour of oxygen were sufficient to reach this temperature, as seen in Table 3.2.3-1.

In Aspen Plus, the calciner unit was modeled using the RK-SOAVE property method with a RGibbs reactor as this model provided the most accurate representation based on the thermodynamic information available on calcium carbonate decomposition. The benefit of using RGibbs modeling is the ability to predict mass and energy balances via thermodynamic databases. This allows the user to input the desired operating conditions and Aspen provides an analysis of the products as if the reactions were allowed to come to complete equilibria, or in this case full conversion of $CaCO_3$. Alas, an evaluation of the modeled data against experimental pilot plant data is essential to ensure the model is accurately describing the system. To do so, the modeled product flowrates were adjusted to replicate the conversion given from Carbon Engineering's data as seen in Table 3.2.3-2 below. It was assumed that the combustion of methane goes to completion, whereas the decomposition of $CaCO_3$ has a 98% conversion. The trace amounts of carbon monoxide produced from incomplete combustion of methane was insignificant and will not alter downstream unit designs.

Table 3.2.3-1 Outlet Flowrate from Calciner

Component	Modeled Flowrate (kmol/hr)	Adjusted Flowrate* (kmol/hr)
$CaCO_3$	0	74.8
CO_2	4738.1	4663.3
CH_4	0	0
O_2	0	0
CaO	3741.5	3666.7
H_2O	1993.3	1993.2
CO	0.03	0.03

*assumes 98% conversion of $CaCO_3$

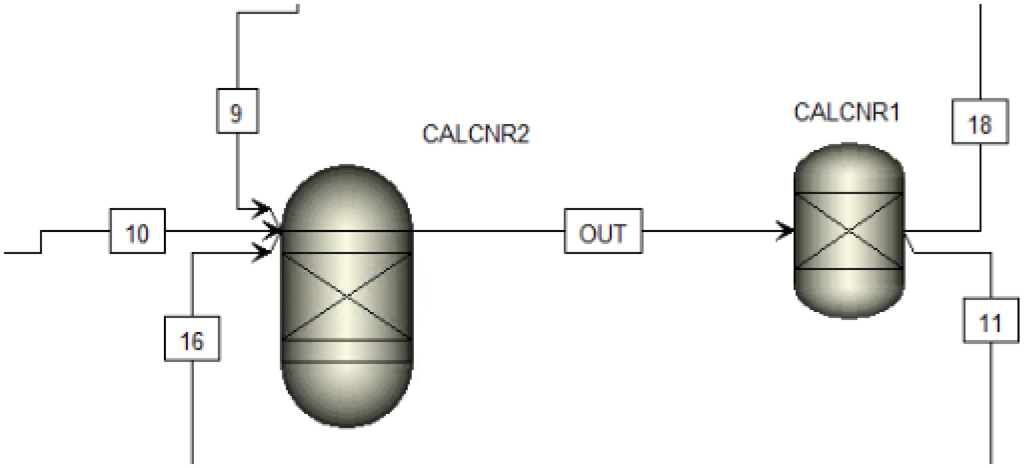


Figure 3.2.3-2 Calciner ASPEN Model

Table 3.2.3-3 Calciner ASPEN Details

Block	**Type**	**Temperature (℃)**	**Pressure (Bar)**	**Heat Duty (MW)**	**Extent of Reaction**
CALCNR1	Sep	898	1	-	-
CALCNR2	RGibbs	898	1	0	0.98

3.2.4. Block 4: Slaker

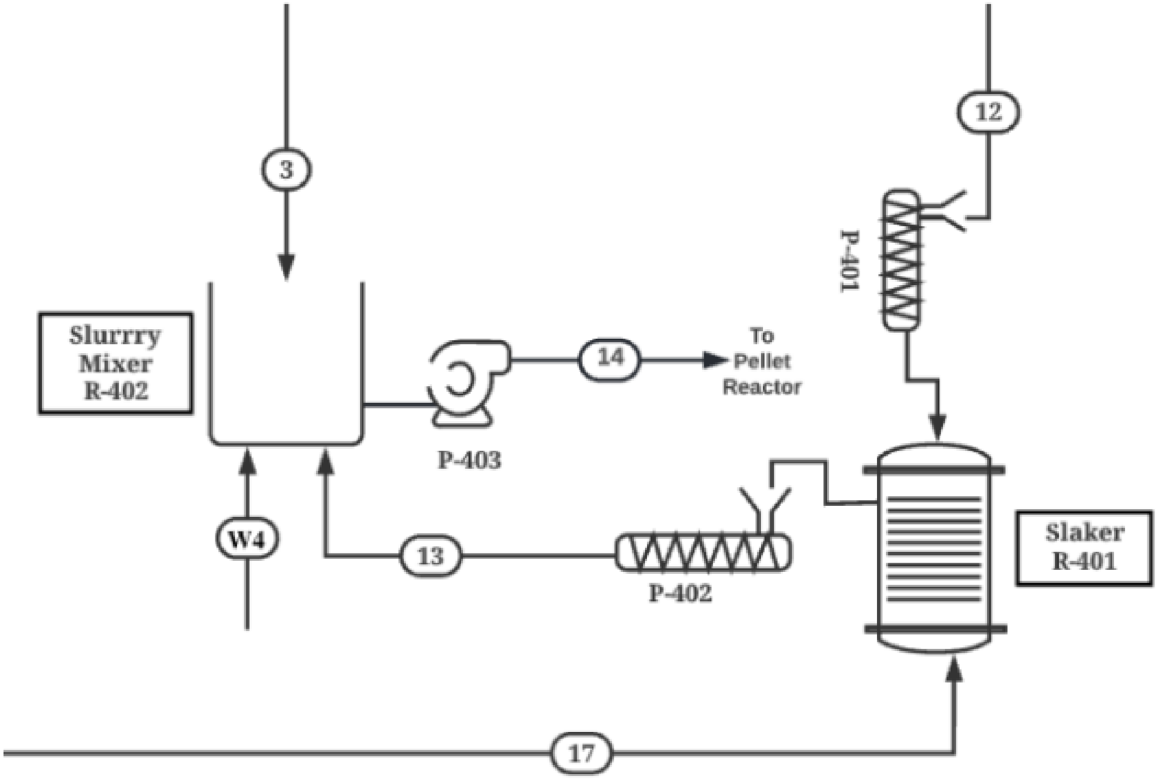


Figure 3.2.4-1 Block 4

Block 4 consists of the slaker reactor, two conveyors, a slurry mixer, and a slurry pump.

Slaker

The purpose of the slaker unit is to hydrate the calcium oxide, or lime, formed in the calciner. This unit functions as a regenerative process to satisfy the calcium hydroxide requirements in the pellet reactor to facilitate the formation of calcium carbonate. The chemical reaction of interest is described in equation 15 below:

$$\text{(Eq. 15)}\ \ CaO_{(s)} + H2O_{(l)} \rightarrow\ Ca(OH)_{2(s)} \quad \Delta H° = -63.9\ kJ\ mol^{-1}$$

Unit Design: This steam slaking process takes place at 300℃ and 1 Bar and in a refractory lined bubbling/turbulent fluid bed, fluidized by recirculating steam flow, as reported by Carbon Engineering (Keith et al., 2018). However, like the air contactor, this unit is blackboxed for this project as designing this process does not fit within time constraints. This unit will still be evaluated via simplified simulations in Aspen Plus as well as via published economic information.

Energy Considerations: The steam slaking process is exothermic. Aspen simulations of this unit showed a heat duty of approximately -89 MW, or if run adiabatically, a product stream that is 300℃ hotter than the reactor temperature. Further heat design considerations should be evaluated if this unit is designed in full, however, this is the extent of the information that will be provided in this report. To this end, no associated utility costs were determined in regard to heat removal for this system.

Material Balances: The material balance was able to be conducted with a reported, experimentally determined extent of reaction of 0.85, published by carbon engineering (Keith et al, 2018). Additionally, after the steam slaking process, the product calcium hydroxide will then be mixed with water to form a 30% calcium hydroxide slurry. Though, the creation of this slurry will be elaborated upon in later reports, refer to **Table 3.2.9-1.**

Aspen Plus Simulations: A simplified slaker unit was modeled in Aspen Plus using an RStoic unit and RK-SOAVE base method. The RStoic unit was utilized as it allowed for the simulation of the chemical reaction under specified conditions including a specified extent of reaction, so the energy evaluations can be representative of the material balance. This was done to understand the energy requirements of the unit, which was elaborated upon earlier in this report. Results of the stream content are reported in the stream tables, see **Table 3.2.9-1.**

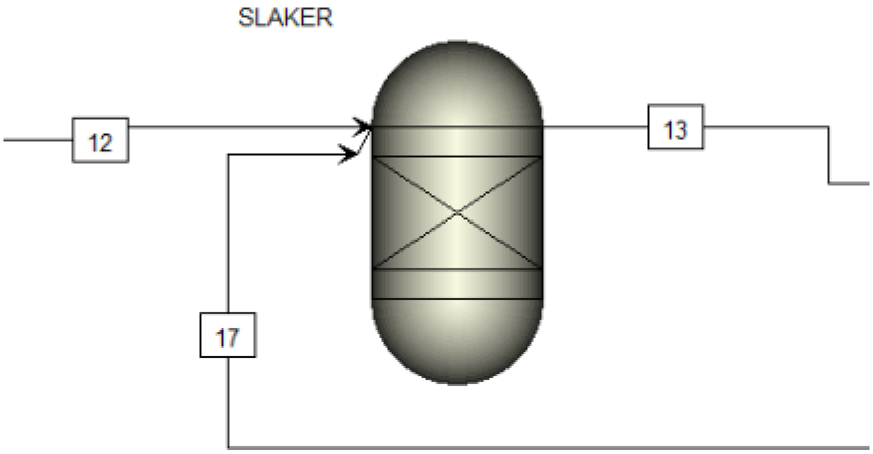


Figure 3.2.4-2 Slaker ASPEN Model

Table 3.2.4-1 Slaker ASPEN Details

Block	Type	Temperature (℃)	Pressure (Bar)	Heat Duty (MW)	Extent of Reaction
SLAKER	RStoic	300	1	-89	0.85

Slurry Mixer

The purpose of the slurry mixer is to create a slurry of calcium hydroxide, or hydrated lime, which will be injected into the bottom of the pellet reactor to facilitate the generation of calcium carbonate pellets. A lime slurry is defined as a suspension of calcium hydroxide in water, and slurries can be made of varying ratios of solid to liquid. In this design, the slurry will consist of 30 wt% calcium hydroxide in water. Slurry mixers are commonly used in water treatment processes where hydrated lime is used as a treating agent for water. In this process, the weight percentage of lime is higher and the caustic flux, not water flux, is optimized which differs from water treatment applications (Keith et at., 2018). Despite the differences, the design choices for the slurry mixer were derived from these traditional applications of slurry mixers.

Using an industry standard of 15 minute resident time for hydrated lime and the total inlet volumetric flowrate into the mixer, the volume of the mixer was found according to the equation below.

$$V = \nu * \tau \qquad \text{(Eq. 16)}$$

where τ is the residence time (s), V is the reactor volume (m^3), ν is the volumetric flowrate (m^3/s)

With this, volume was found to be 107 m^3. Using the volume and an industry standard of height to diameter ratio of 0.8, the diameter and height were found to be 5.6 and 4.4 m, respectively (Griffin, 2009). However, for ease of purchasing sized tanks, these values were rounded to 6 m and 5 m to yield a larger tank with a volume of 141 m^3. Examples of typical impellers used for hydrated lime slurries include pitch turbines, P4-bladed/45° pitched turbines, or hydrofoil impellers. For this application, a 3-blade pitched turbine impeller will be used as it provides the necessary mixing with generally lower power consumptions. Industry standards state that the impeller diameter and baffle width should be one-third and one-twelfth of the tank diameter; therefore, the designed impeller diameter and baffle width will be 2.0 m and 0.5 m, respectively (Griffin, 2009). Typical slurry mixers use four baffles, so four baffles will be used in the designed mixer (Griffin, 2009).

The power consumption was found using the Zwietering correlation, Reynolds number, and Power number calculations. First, the “just-suspended” impeller speed was calculated using the Zwietering correlation shown below.

(Eq. 17) $$N_{JS} = sv^{0.1}\left(\frac{g\Delta\rho}{\rho_L}\right)^{0.45} X^{0.13} d_p^{0.2} D^{-0.85}$$

Where N_{JS} is “just-suspended” impeller speed (s^{-1}), s is the Zwietering geometrical constant, v is the liquid dynamic viscosity (kg/m*s), $\Delta\rho$ is solid-liquid density difference (kg/m^3), ρ_L is liquid density (kg/m^3), X is solid to liquid mass percentage, d_p is particle diameter (m), D is impeller diameter (m), g is acceleration due to gravity (m^2/s)

From this calculation, the impeller speed was found to be 1.20 s^{-1} and can be used to calculate the Reynold’s number of the agitator. This equation is shown below.

(Eq. 18) $$Re = \frac{ND^2\rho}{\mu}$$

Where Re is Reynold’s Number, N is impeller speed (s^{-1}), D is impeller diameter (m), ρ is liquid density (kg/m^3), μ is fluid kinematic viscosity (kg/m*s)

The Reynold’s number associated with the designed agitator was found to be $4.9 \cdot 10^9$, indicating a turbulent flow within the mixer. The Reynold’s number can then be used to find the power number via a correlation plot between Reynold’s number and power number, N_p, found experimentally. This plot is shown in Appendix B in Figure A.B-1. Assuming the trend continues into Reynold’s numbers greater than 10^5, the power number was taken to be 6 with four baffles.

The density of the slurry, which has a direct effect on power consumption, was found via Equation **19**. The power consumption was then found via Equation **20**.

(Eq. 19) $$\rho_{slurry} = \frac{100}{\frac{c_w}{\rho_s} + \frac{100 - c_w}{\rho_L}}$$

Where ρ_{slurry} is slurry density (kg/m^3), c_w is solid concentration percentage by weight, ρ_L is liquid density (kg/m^3), ρ_s is solid density (kg/m^3)

(Eq. 20) $$P = N_p \rho_{slurry} N^3 D^5$$

Where P is power (J/s), N_p is power number, ρ_{slurry} is slurry density (kg/m^3), N is impeller speed (s^{-1}), D is impeller diameter (m)

With this, the calculated power consumption of the slurry mixer was found to be 404 kW.

3.2.5. Block 5 - Water Knockout

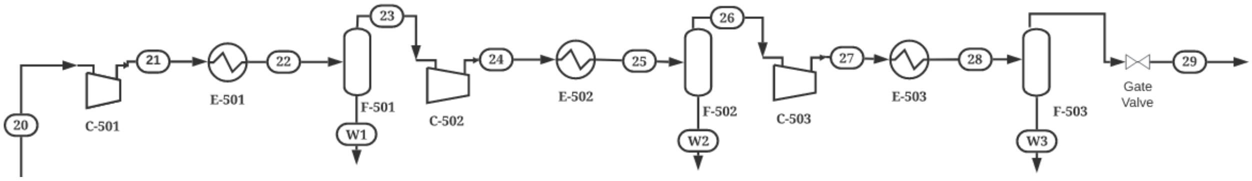


Figure 3.2.5-1 Block 5

Block 5 consists of the "water knockout" system, serving to remove water from the product carbon dioxide stream coming from the Calciner. This block consists of three compressors, three coolers, and three flash drums.

Compressors

In the water knockout system, a set of three compressors are used to increase the pressure of the water vapor and carbon dioxide stream to be later cooled such that water will condense out of the stream. This system achieves an increase in carbon dioxide purity from 57% to 99.8%. All compressors were designed in Aspen Plus as isentropic compressors, modeled with a 3.5 pressure ratio. These parameters were chosen based on reference literature and their Aspen simulations of a similar system (Bianchi, 2018). Each compressor is also designed with an 80% mechanical efficiency as it is a standard value, Aspen Plus simulations showed an overall efficiency of 72%. In actuality, for costing purposes, the compressors will be centrifugal compressors. Data for each compressor can be seen in **table 3.2.5-1.**

Table 3.2.5-1 - Compressor Data for Water Knockout

Compressors	Net work (MW)	Efficiency	Mechanical Eff.	Outlet Pressure (Bar)	Pressure Ratio	Outlet Temp
C-501	27.5	0.72	0.8	3.5	3.5	707.2
C-502	13.4	0.72	0.8	12.25	3.5	245.4
C-503	8.2	0.72	0.8	42.875	3.5	176.3

Of note, the duty of the first cooler is very large; this duty could be lowered by adding a cooling unit before the first compressor, optimizing the water knockout system.

Coolers

Coupled with each compressor is a cooler to allow water vapor to condense given high pressure and low temperature while leaving carbon dioxide as a vapor. Each cooler was modeled in Aspen with a heater block. However, this cooling will be achieved via a cold water stream incoming at 30℃ and leaving the cooler at 45℃, as is commonplace in industry

Amount of cooling water needed for each cooler was found via analysis of duty and temperature change, as simulated in Aspen plus, and Eq. 21.

$$\text{(Eq. 21)} \qquad m_{Cooling\ Water} = \frac{Q}{C\Delta T}$$

Where $m_{\text{Cooling Water}}$ (kg) is the mass flowrate of cooling water, Q is the heat duty of the cooler (W), C is the specific heat of the compounds (W/K•C), and ΔT is the change in temperature between the outlet and inlet of the cooler (℃)

Each cooler in the system is working under differing conditions and flowrates vary. Data for each cooler, including amount of cooling water needed, is provided in table

Table 3.2.5-2 - Cooler Data

Cooler	Duty (MW)	Temp In (℃)	Temp Out (℃)	Pressure In (Bar)	Mass Flowrate Cooling Water (Kg/s)
E-501	54.6	30	45	3.5	871.0
E-502	36.5	30	45	12.3	581.8
E-503	9.3	30	45	42.9	148.1

Flash Drums

The last piece of equipment needed in the water-knockout system is a flash drum to separate the liquid water from the vapor phase. As a flash is needed after each cooler, three will exist in Block 5 to achieve high purity.

To calculate the size of the flash drums, the Souders-Brown equation was used. This equation uses maximum allowable vapor velocity in a separation vessel to determine sizing. Additionally, to find the length of the flashdrum, a ratio of 2.5D:1L was applied, per industry standard. Flashdrum parameters were found from the following equations (Eqn. 22, 23, 24, 25) and reported in table 3.2.5-3.

$$\text{(Eq. 22)} \qquad u = (k)\sqrt{\frac{\rho_L - \rho_V}{\rho_L}} \qquad \text{(Eq. X)}$$

$$\text{(Eq. 23)} \qquad A = \frac{V}{v} \quad \text{(Eq.X)}$$

(Eq. 24) $D = \sqrt{\frac{4A}{\pi}}$ (Eq.X)

(Eq. 25) $L=2.5D$

Where u is the maximum allowable vapor velocity (m/s), V is the vapor volumetric flowrate (m^3/s), A is the cross-sectional area of the flash drum (m), D is the diameter of the flashdrum (m), and L is the length of the flashdrum (m)

Table 3.2.5-3 - Flashdrum Data

Drum	ρ_L(kg/m^3)	ρ_V (kg/m^3)	V (m^3/s)	v	A (m^2)	D (m)	L (m)	Purity
F-501	918.3	4.2	15.4	1.6	9.8	3.5	8.8	0.64
F-502	974.6	21.4	2.7	0.7	3.7	2.2	5.5	0.993
F-503	979.8	91.2	0.6	0.3	1.9	1.5	3.9	0.998

From the flash, excess water will be sent to the water makeup stream entering into the slurry mixer. This accounts for ~1983 kmol/hr of the required make-up water.

Of note, after the flash, a valve can be placed to reduce the outlet stream from 42 Bar to 10 Bar to be sent to methanol synthesis. One point of potential optimization for this project would be to reconsider the water knockout system entirely. Instead, one could re-evaluate the methanol synthesis reactor and design it such that excess water from the upstream process is allowable. Therefore, only pressurizing the stream rather than cleaning the stream could be sufficient. See **Figure 3.2.5-2** for the Aspen Plus configuration.

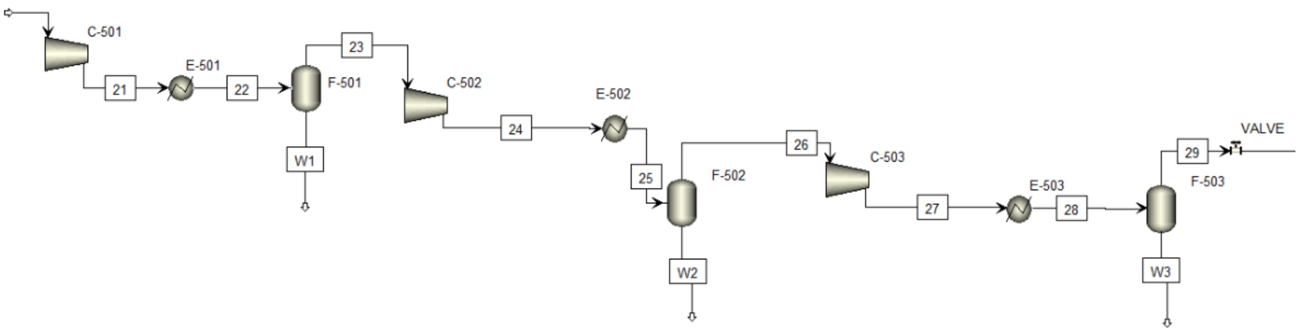


Figure 3.2.5-2 Water Knockout ASPEN Model

3.2.6. Block 6 - Power Island and Oxygen Plant

The final block in the direct air capture system is denoted as “Block 6” and consists of a power island and oxygen plant, which will be blackboxed in its entirety. Due to limitations in scope, this report will not design all aspects of these processes, meaning they are “blackboxed”. While some units are partially blackboxed, like the air contactor and the slaker reactors, some blocks are completely blackboxed. The following sections seek to describe the completely blackboxed portions of the DAC process.

The first blackboxed component is the “Power Island." As described in the Carbon Engineering’s plant report, the power island consists of a natural gas turbine and a heat recovery system generator (Keith et al., 2018). This system will provide power to the different units and equipment in the DAC process. In Carbon Engineering’s report, heat recovery systems are designed to create additional steam to contribute to the turbine. Additionally, all combusted fuel from the turbine will be sent to carbon dioxide absorbers to ensure no carbon dioxide is emitted from the process. The carbon dioxide absorber will also be blackboxed in this design report. All amounts of fuel and products of the turbine process will not be evaluated. While it is assumed that electricity will be supplied by this power island, utilities of the process are still calculated and costed for reference. Of note, this power island is the source of steam for the slaker unit, however, the cost of steam was also found. Future design could include this power island for further understanding of its contribution to the process.

To supply the necessary oxygen to the calciner, an oxygen plant will be required. An oxygen plant consists of a conventional cryogenic air separation unit which is reported to yield a purity of 99.8% (Keith et al., 2018). Based on primitive economic evaluations, purchasing oxygen from an outside vendor exceeds the equipment and operating costs of running an oxygen plant such as this. The oxygen plant will supply stream 10 with pure oxygen, and this part of the process will also be blackboxed with no design considerations beyond this. However, the reported capital cost as well as electrical consumption will be included in economic evaluations.

3.2.7. Direct Air Capture Heat Exchanger Design

The direct air capture system requires considerations in regards to the heat design. Specifically, a heater (E-201) is needed to heat calcium carbonate traveling from the pellet reactors to a series of cyclone heat exchangers (E-301, E-302). Then, an additional cyclone heat exchanger (E-303) is needed to cool calcium oxide flowing from the pellet reactor and heat oxygen entering into the calciner. For reference, see **Figure 3-2.**

There is an added component of complexity as heat exchange in this process occurs between solid and gas phases. There are a few options for gas-solid heat exchangers, for example, cyclone, packed bed and rotary drum heat exchangers. For this process, cyclone heat exchangers were chosen as this type of heat exchanger was used in the process constructed by reference DAC plants and there is literature to support this choice for gas-solid heat exchange. Cyclones have historically been used for separation processes involving particles, but more recently cyclones have been researched as heat exchangers for solid and gas phases (Jain, 2006). Cyclones as heat exchangers typically are large steel vessels lined with refractory bricks where pellets and gas streams are in direct contact with each other (Keith, 2018). A schematic of a cyclone heat exchanger is shown below in Figure 3.2.7-1.

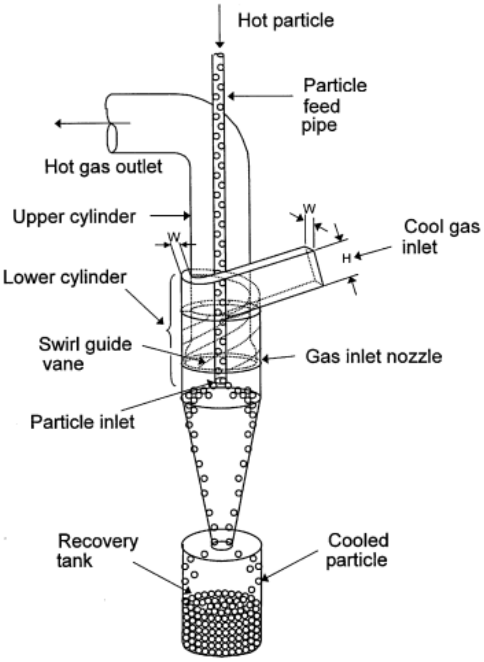


Figure 3.2.7-1 Example Schematic of a Cyclone Heat Exchanger

Modeling Via Aspen Plus: All heat exchangers were modeled using the HeatX model through Aspen Plus simulations. The HeatX model was chosen as it models a two stream heat exchanger in which the exchanger geometry is not known initially. The calculation mode chosen was *Shortcut* as this mode can perform the necessary material and energy balances without input information about the geometry of the exchanger ("Heat Exchangers in Aspen Plus," n.d.).

When deciding the flow direction (i.e. co-current, countercurrent, multipass), it is necessary to analyze how the heat exchanger being modeled operates in real operation and how the passing streams interact with each other. Cyclone heat exchangers act similarly to co-current heat exchangers as both streams flow in the same direction which is illustrated in Figure 3.2.7-1.

Heater- E-201

The purpose of the heater, E-201, is to increase the temperature of calcium carbonate pellets exiting the pellet reactor from 27°C to 300℃. The heater, E-201, is designed as a fired heater, also known as a furnace. The calcium carbonate pellets will leave the pellet reactor with some amount of water entrained. For the purposes of this research, it is assumed that the pellets entering the heater have no entrained water and the stream is purely calcium carbonate. In real operation, the slurry that exits the reactor would be drained using a filter to remove the majority of the water and heated above 100℃ to evaporate the residual water. Therefore, the heat duty calculated will be lower than real operation, but sufficient for this design basis. With that, the required energy to heat the stream of calcium carbonate pellets from 27℃ to 300℃ was found to be 23.7 MW.

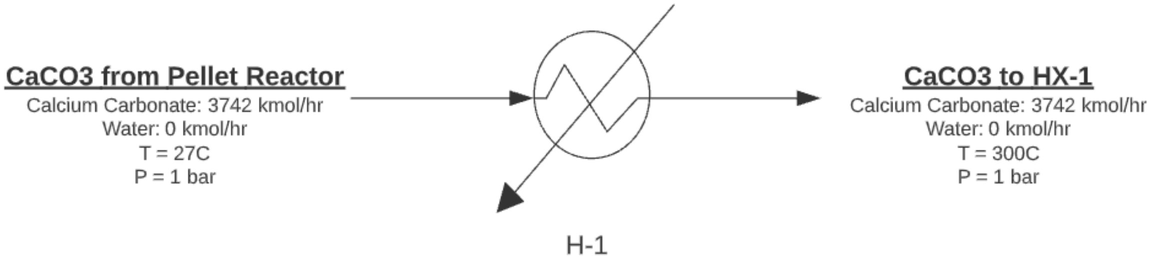


Figure 3.2.7-2 Schematic of Heater (E-201)

Heat Exchangers Design - E-301 & E-302

In order to heat the calcium carbonate pellets from 300℃ to 646℃ to reach the proper feed conditions for the calciner, heat exchange will occur with the gas stream leaving the calciner, exiting at a temperature of 898℃. The gas stream, composed of mostly carbon dioxide and water vapor, will be cooled in this process to a temperature of about 460℃. To facilitate this heat transfer, two co-current heat exchangers are necessary to avoid having a scenario where the outlet cold stream exits at a higher temperature than the outlet hot stream. This hypothetical violation of thermodynamics can be seen in Figure 3.2.7-3.

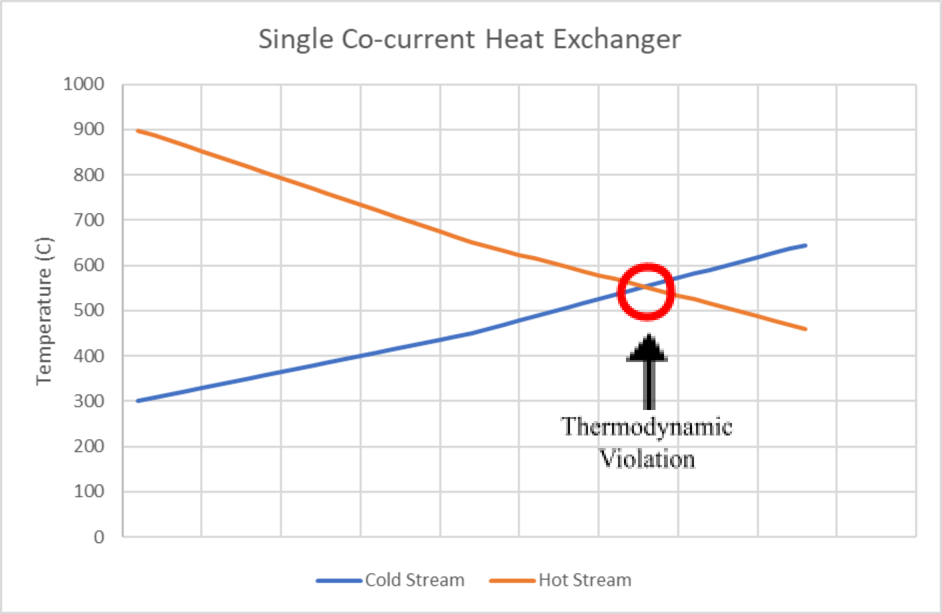


Figure 3.2.7-3 Temperature Profile of Single Co-current Heat Exchanger

To circumvent the issue, two co-current heat exchangers will be designed in series to model the system. The calcium carbonate pellets exiting heater, E-201, are fed into Heat Exchanger, E-301, to be heated from 300℃ to 450℃ and immediately fed into heat Exchanger, E-302, to be heated from 450℃ to 646℃. The gas stream leaving the calciner at 898℃ is fed into E-302 to be cooled to 650℃. Finally, the gas stream exiting E-302 is fed to E-301 to be cooled to 461℃ and then is sent to a series of compressors that have yet to be designed. The calculated heat duties for E-301 and E-302 were found to be 16.7 and 23.2 MW, respectively. The dual heat exchangers are illustrated in Figure 3.2.7-4 below.

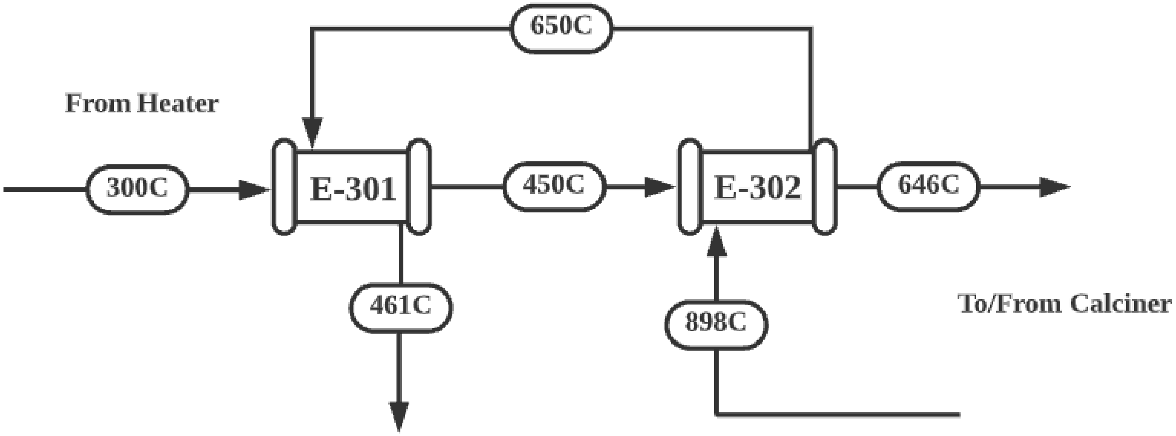


Figure 3.2.7-4 Schematic of Dual Co-current Heat Exchangers (E-301 & E-302)

Additionally, the TQ curves showing the relationship between the temperature profile and heat transferred for each heat exchanger are shown in **Figure 3.2.7-5**.

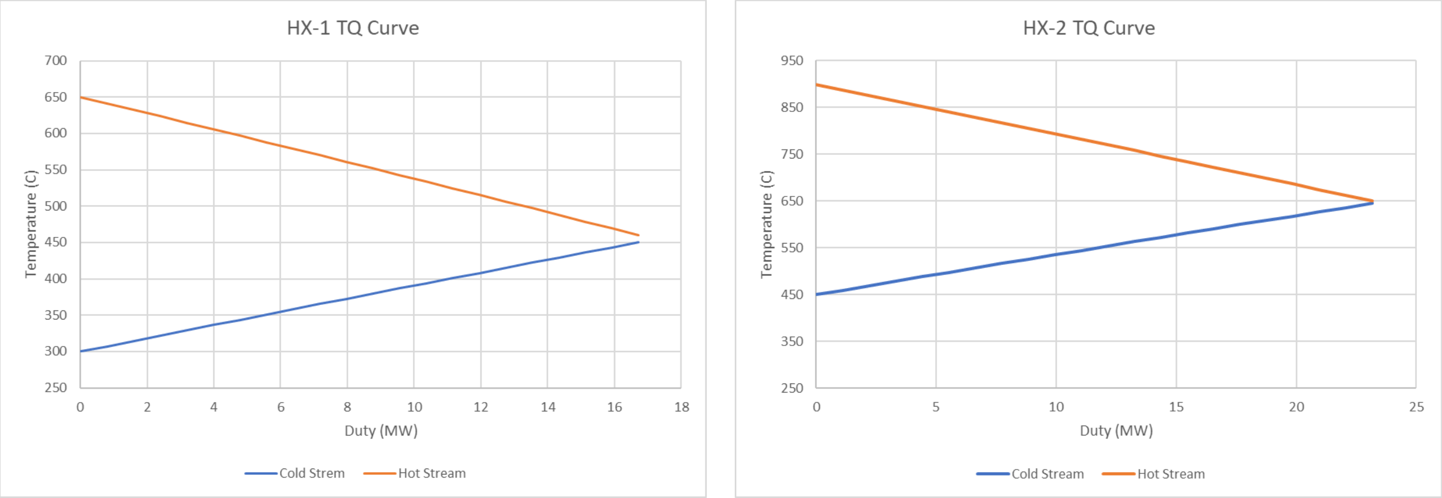


Figure 3.2.7-5 TQ Curves for HX-1 and HX-2

Heat Exchanger Design - E-303

The purpose of the Heat Exchanger, E-303, is to preheat the oxygen fuel for the calciner from 21℃ to 250℃ via heat transfer with the stream of calcium oxide pellets exiting the calciner. The calcium oxide pellets are fed into the heat exchanger at 898℃ and exit at a lower temperature of 837℃. The equivalent heat duty of E-303 was calculated via Aspen to be 3.8 MW. An illustration of the heat exchanger is shown below in Figure 3.2.7-6.

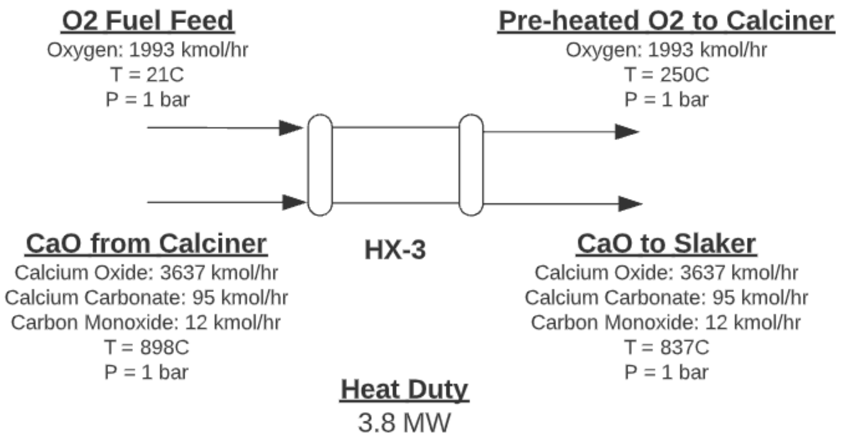


Figure 3.2.7-6 Schematic of Heat Exchanger 3 (E-303)

Cyclone Design

To evaluate the heat exchanger design as a cyclone heat exchanger the total required heat transfer surface area was determined from Equations 26-28. Due to lack of information about the components in the system, the heat transfer coefficient for air in a forced-convection system was used. For all heat exchangers this value was calculated and reported in Table 3.2.7-1.

$$\text{(Eq. 26)} \qquad \Delta Tm = \frac{\left(T_{Gin} - T_{Sin}\right) - \left(T_{Gout} - T_{Sout}\right)}{\ln ln\left(\frac{T_{Gin} - T_{Sin}}{T_{Gout} - T_{Sout}}\right)}$$

$$\text{(Eq. 27)} \qquad Qt = m_s c_{ps}\left(T_{Sout} - T_{Sin}\right)$$

$$\text{(Eq. 28)} \qquad At = \frac{Q}{h \cdot \Delta T}$$

Where ΔTm is the log-mean temperature difference (K), T_g is the temperature of the gas stream (℃), T_s is the temperature of the solid stream (℃), Q is the heat transfer rate (J), m_s is the mass of the solid, c_{ps} is the specific heat of the solid, A is the heat transfer area (M^2), and h is the heat transfer coefficient ($W/(m^2K)$).

Next, the diameter of the cyclone was approximated using correlations reported in "Studies on Gas-Solid Heat Transfer in Cyclone Heat Exchanger" by Jain et al. This paper reported correlations for a heat exchanger cyclone system that exchanged heat between air and cement particles. Due to the complexity and lack of information regarding cyclone heat exchangers, this correlation was assumed to be sufficient. Again, the heat transfer coefficient was approximated to be air in a forced-convection system. Results of the diameters for each heat exchanger are reported in Table 3.2.7-1.

Equation 34 is the final equation utilized to determine diameters, however, equations 29 through 33 were substituted in when necessary for final calculations.

$$\text{(Eq. 29)} \qquad Nu = 1300 \cdot Re^{0.41} F_m^{0.47}\left(\frac{2 \cdot d_p}{D_c}\right) Pr^{\frac{1}{3}}$$

$$\text{(Eq. 30)} \qquad Nu = \frac{h_p D_c}{k_a}$$

$$\text{(Eq. 31)} \qquad Re = \frac{\vartheta_c D_c \rho_g}{\mu_g}$$

$$\text{(Eq. 32)} \qquad Pr = \frac{c_{pa} D_c \mu_g}{k_g}$$

(Eq. 33) $$F_m = \frac{m_s}{m_a}$$

(Eq. 34) $$D_c = \sqrt[2.41]{\frac{1300 \cdot \left(\frac{4\dot{V}\rho_g}{\pi\mu_g}\right)^{0.41} F_m^{0.47} \cdot 2 \cdot k_g D_p Pr^{1/3}}{h_p}}$$

(Jain et al.)

Where Nu is the Nusselt number, Re is the Reynolds number, Fm is the solid loading ratio, d_p is the diameter of the solid, D_c is the diameter of the cyclone heat exchanger (m), Pr is the Prandtl number, h_p is the gas- particle heat transfer coefficient (W/m^2K), k_g is the thermal conductivity of the gas (W/mK), υ is the cyclone inlet velocity of gas, ρ_g is the density of gas (kg/m^3), μ_g is the dynamic viscosity of the gas (Pa S)

Table 3.2.7-1 Heat Exchanger Dimensions Results

	E-301	**E-302**	**E-303**
Streams Interacting	CaCO3\CO2	CaCO3\CO2	CaO\O2
Heat Transfer Rate (W)	$8.47 \cdot 10^{10}$	$1.11 \cdot 10^{11}$	$4.29 \cdot 10^{10}$
Req. Heat Transfer Area (m2)	$3.46 \cdot 10^{6}$	$4.71 \cdot 10^{6}$	$4.56 \cdot 10^{5}$
Cyclone Diameter (m)	2.92	2.92	1.36

3.2.8. Pump and Conveyor Design

Pumps: In the DAC process, there is a need to transport liquids such as potassium hydroxide, potassium carbonate, and calcium hydroxide slurry between unit operations. For the process, three pumps, P-101, P-102, and P-403, were designed to accomplish this. Pump, P-101, transports the capture solution, potassium carbonate, from the air contactor to be mixed in the slurry mixer before then entering the pellet reactor. The slurry leaving the slurry mixer is then transported to the pellet reactor via pump, P-403. To supply the air contactor with potassium hydroxide, pump, P-102, transports the regenerative solution from the pellet reactor back to the air contactor. The constant circulation of fluid between the air contactor and pellet reactor allows for a continuous capture of carbon from ambient air.

The pumps will be centrifugal pumps which are commonly used in industrial applications, such as the DAC process. Frictional losses within the pipes and for each control valve associated with the pumps account for 51 kPa each. Pumps, P-102 and P-403, are designed to transfer the fluids to varying heights which contributes to the associated gravity head for each pump. To supply the air contactor, pump, P-102, will transport the fluid 20 meters vertically, which is the reported highest point of Carbon Engineering's air contactor system (Keith et al., 2018). The pump, P-403, will transport the slurry 7 meters vertically to ensure that the slurry reaches the highest point of the pellet reactor. To account for inefficiencies within the pumping system, mechanical and electrical efficiencies were assumed to be 70% and 90%, respectively, to give the adjusted electrical draw. The operating conditions of the pumps are illustrated in the table below.

Table 3.2.8-1. DAC Pump Operating Conditions

Pump	Total Frictional Losses (kPa)	Gravity Head (kPa)	Differential Pressure (kPa)	Hydraulic Power (kW)	Electric Draw (kW)
P-101	101.3	0	101.3	50.6	80.4
P-102	101.3	240.3	341.7	183.2	290.8
P-403	101.3	90.4	191.8	110.8	175.9

Conveyors:

In the DAC process, much of the material that must be transported between units is in the solid phase. These materials include the calcium carbonate pellets, the CaO that is produced in the calciner, and the $Ca(OH)_2$ that is formed in the Slaker. Therefore, conveyor systems must be used as opposed to pumps. For this process, closed-loop pneumatic conveyors were chosen as they are standard solid transport units used in industry. Additionally, as many streams are at high temperatures, the pneumatic component can help with cooling if necessary.

As the scope of this report is limited, the pneumatic conveyor design is limited. This report assumes that all conveyors will be 50m long for sizing and economic evaluations were found from published correlations. In total, six conveyors will be needed. Each conveyor as well as its purpose is provided in the table below.

Table 3.2.8-2 DAC Conveyor Descriptions

Conveyor ID	Purpose
P-201	Transport $CaCO_3$ pellets from Pellet Reactor (R-201) to Heat Exchanger (E-301)
P-301	Transport $CaCO_3$ pellets from E-301 to E-302
P-302	Transport $CaCO_3$ pellets from E-302 to Calciner (R-301)
P-303	Transport CaO from calciner to E-303
P-401	Transport CaO from E-303 to Slaker (R-401)
P-402	Transport $Ca(OH)_2$ from Slaker (R-401) to Slurry Mixer (R-402)

3.2.9-1 DAC Process Stream Table

Table 3.2.9-1: Direct Air Capture Process Stream Table

Direct Air Capture Process Stream Table (kmol/hr)																		
Stream #	CO_2	O_2	N_2	KOH	K_2CO_3	$CaCO_3$	CaO	$Ca(OH)_2$	CH_4	CO	H_2O	H_3O^+	K^+	HCO_3^-	OH^-	CO_3^{2-}	$Ca(OH)^{2+}$	Ca^{2+}
1	4118.5	2171288.4	8191412.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	164381.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	451.8	2171288.3	8191412.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	175930.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	0.0	0.3	0.6	0.0	3745.4	0.0	0.0	0.0	0.0	0.0	89634.6	0.0	9900.0	522.9	5.1	3849.6	0.0	0.0
4	0.0	0.0	0.2	7483.0	0.0	0.0	0.0	0.0	0.0	0.0	98145.9	0.0	9900.0	0.1	6710.9	1594.5	0.0	0.0
5	0.0	0.1	0.3	0.3	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6	0.0	0.0	0.0	0.0	0.0	3741.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
7	0.0	0.0	0.0	0.0	0.0	3741.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	0.0	0.0	0.0	0.0	0.0	3741.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0	0.0	3741.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	996.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.0	0.0	74.8	3666.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0	0.0	74.8	3666.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
13	0.0	0.0	0.0	0.0	0.0	74.8	550.0	3116.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
14	0.0	0.0	0.0	0.0	0.0	74.8	0.0	3666.7	0.0	0.0	16901.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
15	0.0	1993.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
16	0.0	1993.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3666.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
18	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1993.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
19	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1993.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1993.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
21	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1993.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
22	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1993.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
23	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1681.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
24	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1681.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
25	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1681.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
26	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	32.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
27	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	32.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
28	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	32.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
29	4663.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
W1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	310	0.0	0.0	0.0	0.0	0.0	0.0	0.0
W2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1648.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
W3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	22.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
W4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	17451.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0

3.3. Methanol Synthesis Design

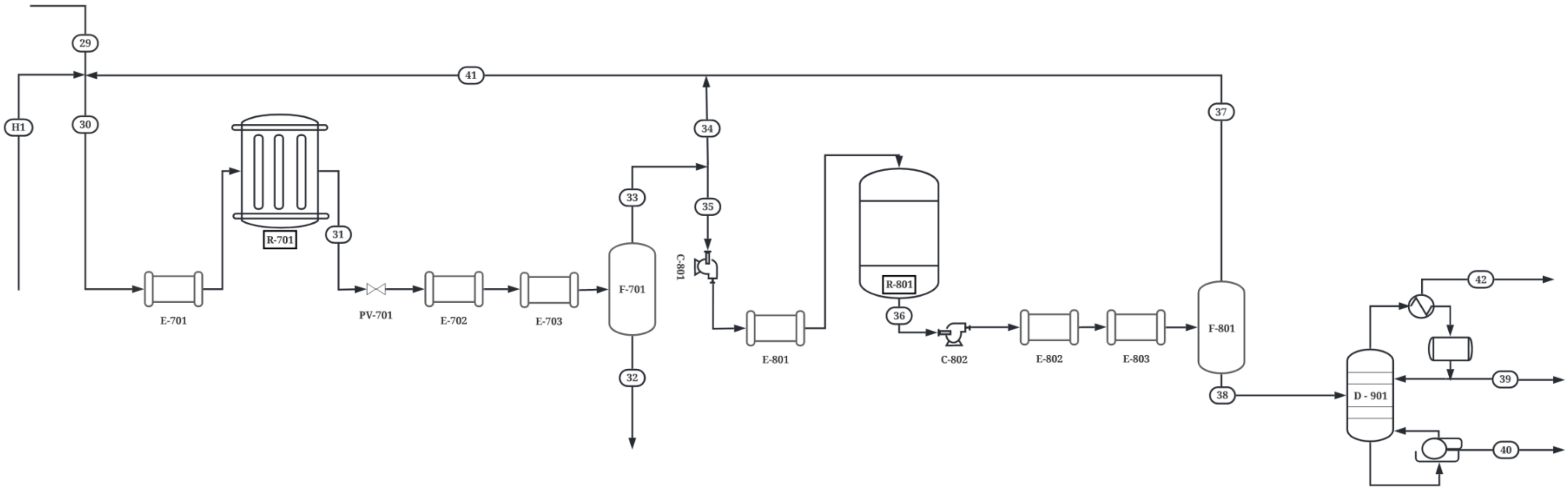


Figure 3.3-1 Overall Methanol Production Process Flow Diagram

3.3.1. Block 7: Reverse Water Gas Shift

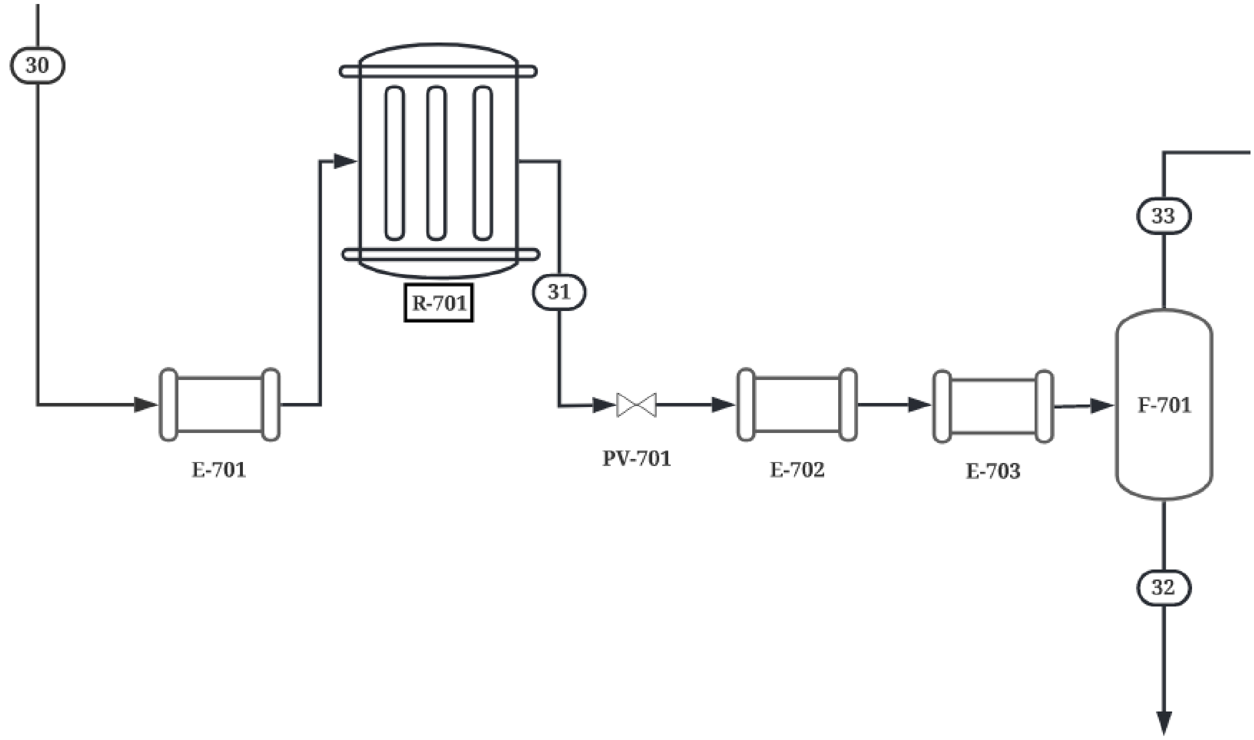


Figure 3.3.1-2 Block 7

Block 7 consists of the main reverse water gas shift reactor, five pumps, and a condenser. Of note, the heat exchanger E-701 will be described in its dedicated section.

Reverse Water Gas Shift

The primary function of the reverse water gas shift reactor is to perform a catalytic reduction of carbon dioxide to carbon monoxide. To achieve this, a carbon dioxide feedstock will be received from the direct air capture upstream process and contact a feed of hydrogen gas purchased from a third-party source. The carbon monoxide gas produced will then be sent to the methanol synthesis reactor in the downstream portion of this process. The primary reaction taking place in the reverse water gas shift reactor is as follows:

$$\text{(Eq. 34)}\quad CO_{2\,(g)} + H_{2\,(g)} \rightarrow CO_{(g)} + H_2O_{(g)} \quad \Delta H^\circ = +41.3 \text{ kJ/mol}$$

Unit design: The reactor chosen is a heterogeneous packed bed reactor that consists of 12,568 individual reactor tubes. A heterogeneous packed bed was selected as a reactor of choice, as catalytic reactors are standard use in industry for catalytic processes involving gaseous streams. The reactor will run at operating conditions of 500℃ and at 10.1 Bar. These operating conditions are based on a pilot plant and modeling data of the CAMERE (carbon dioxide hydrogenation to form methanol via a reverse water-gas-shift reaction) process by the Korean Institute of Science and Technology (Oh-Shim Joo, 1999). This reactor contains multiple tubes to increase the amount of surface area for sufficient heat transfer to take place. Each reactor tube will have a height of 2 meters and a tube diameter of 0.05 meters. This reactor was designed to have a fractional conversion rate of 61.2% for carbon monoxide, as consistent with the data presented by the pilot plant.

This reaction will require a catalyst in order for the desired product of the system, carbon monoxide, to be produced. The chosen catalyst utilized is ZnO/Al_2O_3 (1:2) due to its durability and longevity (Joo, 2003). Additionally, this catalyst presents a high carbon monoxide selectivity throughout the operation of the reactor (Joo, 2003). The catalyst diameter was determined to be 0.025 meters, as supported by current catalyst industry standard diameters. The amount of catalyst required is approximately 74,027 kilograms, as determined by the amount of catalyst used in the pilot plant. This mass of catalyst is the annual use for this reactor. The catalyst activity period, the amount of time the fractional conversion was above the specified 61%, was recorded to be 210 hours for a conversion rate of 60% in the pilot reactor. So, it was assumed the activity of the catalyst would be scaled up to a total activity period of approximately 2,000 hours. Therefore, a regeneration period of the catalyst could be implemented when downtimes occur in the plant process.

Energy Analysis: This reaction is mildly endothermic and therefore will require an input of heat. The necessary heat duty to achieve the reaction was found to be approximately 57.5 MW, as was determined by Aspen Plus simulations. A steam flow will be used to provide the required heat, at a flowrate of 5093 kmol/hr.

Modeling Via Aspen Plus: The reverse water gas shift reactor was modeled through Aspen Plus using an RGibbs reactor and the property package RK-ASPEN. The RGibbs reactor model was selected to determine the heat duty required, as the reaction will converge to equilibrium. RK-ASPEN was selected as the property package as the reactor streams include hydrocarbons, polar components, alcohols, and gaseous streams.

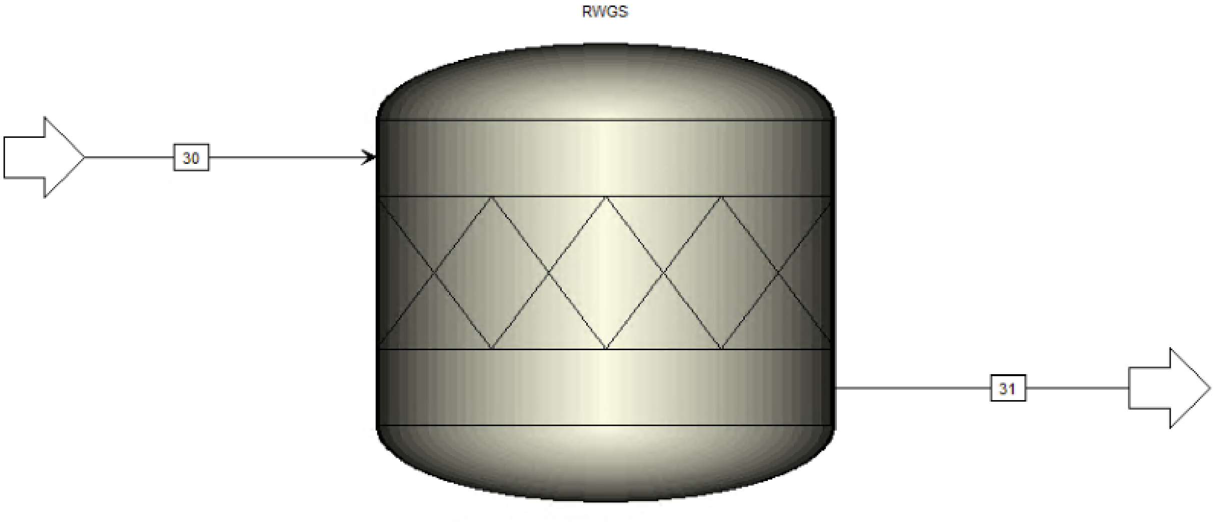


Figure 3.3.1-3 Reverse Water Gas Shift Reactor ASPEN Model

Table 3.3.1-1 Reverse Water Gas Shift Reactor ASPEN Details

Block	Type	Temp (C)	Pressure (Bar)	Heat Duty (MW)	Extent of Reaction
RWGS	**RGibbs**	500	10.1325	57.5	0.61

Material Balances: The inlet and outlet flowrates were found based on the initial, known feed of CO_2 going into the methanol synthesis process, which is being received from the direct air capture unit, the calciner. Moreover, the overall fractional conversion rates were found in a paper by Joo, O.S, et al, about their research of the CAMERE process. The overall fractional conversion rate of the process was found to be 53% from literature, and the first reactor's fractional conversion rate was found to be 61%. The overall fractional conversion rate is needed due to the recycle flow of CO_2 from the methanol synthesis reactor to the reverse water gas shift. Using this value, a product flow of methanol can be determined solely from the feed of CO_2. After finding the amount of methanol produced, the individual reactor's overall fractional conversions can then be used to find the rest of the streams as necessary. Using both of these conversions to find relevant extents of reactions, flowrates of the streams can be found accordingly, refer to **Table 3.3.5-1.**

Reactor Dimension Calculations

Volume: The total volume required by the reactor was calculated through residence time calculations as shown in equation 35. A residence time of 0.064 seconds is used, a lower residence time increases carbon monoxide selectivity (Daza, 2016). With this information, the total volume of the reactor was found below using the residence time equation below:

$$\text{(Eq. 35)} \qquad \tau = V/v$$

where τ is the residence time (s), V is the reactor volume (m^3), v is the volumetric flowrate (m/s).

Using this equation, the reactor volume was calculated to be 197.4 m^3.

Pressure Drop: The pressure drop through the reactor was calculated by the Ergun Equation:

$$\text{(Eq. 36} \qquad \frac{\Delta p}{L} = \frac{150 u_f \, (1-\epsilon)^2 u_o}{\epsilon^3 d_p^{\,2}} + \frac{1.75(1-\epsilon)\ \rho_s\ u_{fo}^{\,2}}{\epsilon^3 d_p}$$

where Δp is the pressure drop (Pa), L is the length of the reactor (m), μf is the fluid viscosity (N/m^2), ϵ is the void space of the bed (m^3), u_o is the fluid superficial velocity (m/s), d_p is the particle diameter (m), and ρ_s is the fluid density (kg/m^3).

An estimated pressure drop of 0.14 bars was calculated for the reactor. To achieve this minimal pressure drop value, a reactor height of 2 meters was required. The radius was calculated to be 0.05 meters. This radius was determined to keep the radius and height ratio consistent with the pilot plant reactor dimensions (Joo, 2003). Finally, the volume of each reactor was calculated with and to achieve a reactor volume 197.4 m^3, a total number of 12568 reactors was calculated.

Catalyst Requirement Calculations

The amount of catalyst required was calculated through the gas hourly space velocity (GHSV) parameter, which was found from the reference pilot plant data (Oh-Shim Joo, 1999). This design seeks to use the same catalyst as the reference pilot plant, so it was assumed that it is appropriate to keep this value constant in the scale up calculation.

$$\text{(Eq. 37)} \qquad GHSV = \frac{Vo}{Mc}$$

Where Vo represents the exhaust flow (mL/hr), and Mc represents the mass of catalyst (g)

The GHSV value listed is 150,000 ($ml/g_{catalyst} \cdot hr$) and the exhaust volumetric flowrate out, obtained from the material balance, of the reactor was used. Using this equation, the total amount of catalyst required for this reactor was calculated to be 74,027 kilograms.

Condenser

The condenser following this reactor is designed to remove water from the carbon monoxide and hydrogen heavy stream; this allows for a more concentrated stream of gasses for the next reactor.

The first heat exchanger (E-702) in this condenser system produces steam from boiler feed water at an incoming flow rate of 58,613 kmol/hr at 30℃ and 9.1 bars. The required surface area for sufficient heat transfer was determined to be 1,087 m^2. To accommodate this surface area, the heat exchanger requires a total of 3,736 tubes with the industry standard measurements of 5 meters length and 0.02 meters outer diameter. The reactor effluent stream leaves this heat exchanger at 180℃.

Next, a series of heat exchangers (E-703) are used to lower the temperature of the reactor effluent stream down to 35℃. It was determined that running cooling water at 200,000 kmol/hr at a feed temperature of 30℃ would effectively decrease the temperature to the desired value. From the Aspen Plus simulation, the required surface area was calculated to be 8,027 m^2. Current industry standards show that the heat transfer surface area for a single heat exchanger is approximately 1000 m^2. To accommodate this standard, E-703 is designed to have 8 shells in series, with a total of 27,612 tubes across the 8 shells.

The stream leaving the heat exchanger will flow into a flash drum (F-701). This flash drum will allow for 96% of the water to be removed from the effluent stream and the water will simply be waste water, or can be used as cooling water in other processes. The operating conditions of the flash drum does not differ from the operating conditions of the incoming stream. The top product of the flash drum will be split to a recycle stream and feed stream for block 8. The splitter separated the stream in a 6:4 ratio, where 60% of the stream became the recycle stream, and 40% of the stream became the feed stream into block 8. This ratio was chosen as it was the same ratio from the CAMERE process model plant (Joo, 1999). In this calculation, it was assumed that none of the methanol entered the recycle stream.

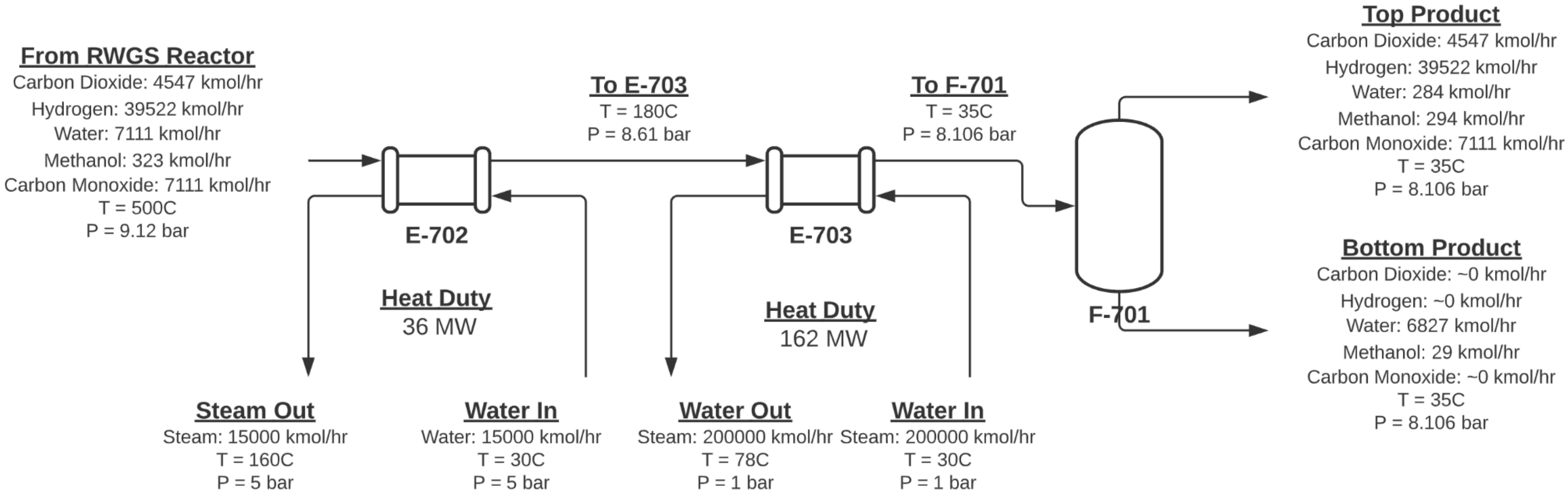


Figure 3.3.1-4 Schematic of the RWGS Condenser

3.3.2. Block 8: Methanol Synthesis Reactor

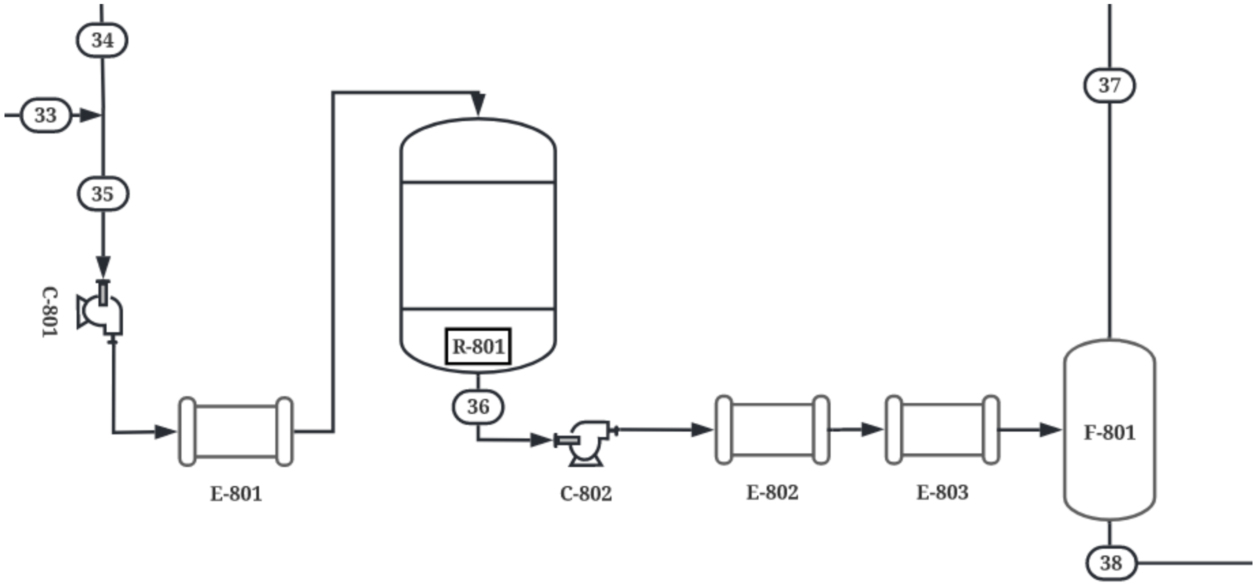


Figure 3.3.2-1 Block 8

Block 8 consists of the main methanol synthesis reactor, six pumps, and a condenser. Heat exchanger E-801 will be explained in a later section.

Methanol Synthesis

The purpose of the methanol synthesis reactor is to utilize the carbon monoxide from the Reverse Water Gas Shift reactor to produce the final product, methanol. This is done through the hydrogenation of the carbon monoxide. This reaction is as follows:

(Eq. 38) $CO_{(g)} + 2H_{2\,(g)} \rightarrow CH_3OH_{(g)}$ $\Delta H° = -91$ kJ/mol

Unit design: The methanol synthesis reactor is a multitube heterogeneous packed bed reactor utilizing $Cu/ZnO/Al_2O_3$ as a catalyst (Joo,1999). This type of reactor was selected to allow for the proper reactor cooling to occur as well as provide an avenue for an adequate amount of catalyst to be used. The reactor will contain a total of 676 tubes with an industry standard length of 7 meters and a radius of 0.1 meters for a total volume of 148.5 m^3. Additionally, a literature review of a pilot reactor for the CAMERE process was done to determine the operating conditions of this reactor; the pilot reactor found that to optimize methanol yield the reactor needed to operate at 250^{o}C and 30.4 bar (Joo, 2003).

The catalyst that will be used to achieve the desired reaction is $Cu/ZnO/Al_2O_3$. Originally, $Cu/ZnO/ZrO_2/Ga_2O_3$, was explored as a potential catalyst as research showed it had a high activity, resulting in a ~15% higher methanol yield compared to traditional commercial catalysts (Joo, 1999). However, due to a lack of available information about the catalyst

$Cu/ZnO/ZrO_2/Ga_2O$, the catalyst $Cu/ZnO/Al_2O_3$ was instead chosen as it is commonly used in industry. The total amount of catalyst needed for the entire methanol synthesis reactor was determined to be 48254 kg based upon the size of the reactor and its GHSV value, 12,000 ($ml/g_{catalyst} \cdot hr$).

The size of current industrial catalysts of this size range from 0.0016 m to 0.016 m diameter spheres, though this process seeks to use 0.016 m spheres to maximize methanol yield (Unicat, 2011). The activity of the catalyst was tested and maintained over 70 hours, therefore, it can be assumed that this catalyst can be used for up to 1000 hours before regeneration is required. As this plant will operate for less time than the standard yearly basis (6000 hours per year) , there will be sufficient time to regenerate the catalyst between operations.

Energy Analysis: This reaction is exothermic, therefore the heat duty was calculated and found to be 68.3 MW via Aspen Plus simulations. For heat removal, a flow of boiler feed water will be used. A boiler feed water flowrate of 6049 kmol/hr is required.

Material Balances: Similarly to the reverse water gas shift reactor, these inlet and outlet flowrates were calculated using the overall conversion rates found in a paper by Joo. O.S. et al. Using the 53% fractional conversion rate for the overall process from literature, the amount of methanol produced was found in a similar process to the material balance for the RWGS reactor. Using this value, along with the 87% fractional conversion rate for the reactor studied, the necessary streams and flows and compositions were found as needed.

Of note, while the current material balance does not account for the production of water in the second reactor from a side reaction of the reverse water gas shift reaction, the amount of water produced is significantly small. Therefore, in the final balances, additional water is not accounted for, refer to **Table 3.3.5-1.**

Modeling Via Aspen Plus: The reactor was modeled as an RStoic reactor with the RK-ASPEN property method. An RStoic reactor was selected so that the conversion rate of 87% of CO from the pilot plant reactor could be maintained.

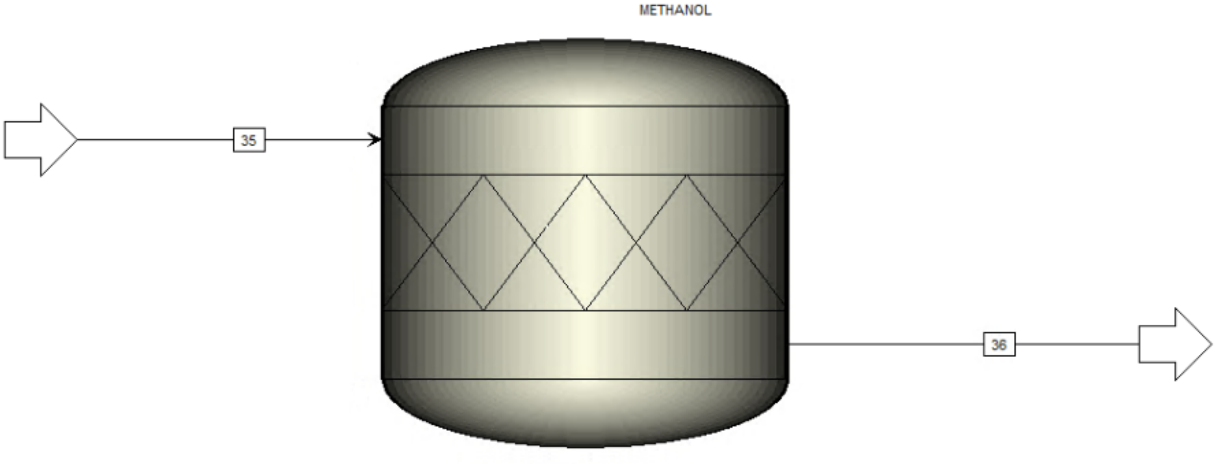


Figure 3.3.2-2 Methanol Synthesis Reactor ASPEN Model

Table 3.3.2-1 Methanol Synthesis Reactor ASPEN Details

Block	Type	Temp (C)	Pressure (Bar)	Heat Duty (MW)	Extent of Reaction
Methanol	**RSTOICH**	250	10.1325	69	0.87

Volume: The scale up of this reactor was performed similarly to the RWGS reactor. The pilot reactor was found to have a residence time of 0.923 seconds, using this information and the volumetric flowrate, equation 35 was used to determine that a volume of 148.5 m^3 was needed for this reactor (Joo, 1999). The length of each tube in the reactor was set to be 7 meters, to follow industry standards, and the diameter was determined by discovering the adequate surface area for the heat transfer of the reactor, see equation 39. The total heat transfer was calculated using Aspen Plus.

$$\text{(Eq. 39)} \quad Q = U \times At \times \Delta T$$

where Q is the heat duty (W), U is the overall heat transfer coefficient (W/m^2 K), At is the surface area of heat transfer (m^2), and $\Delta T$is the temperature difference between the fluids (K)

Heat Transfer: It was decided that boiling water at 150°C will be used as the heat transfer fluid. This will allow for the maximization of heat transfer as well as give us low pressure steam credit. The overall heat transfer coefficient, *U,* was estimated to be 150 W/m^{2}K using equation 40.

$$\text{(Eq. 40)} \quad U = \left(\frac{1}{h_o} + \frac{r_o \ln(\frac{r_o}{r_i})}{k} + \frac{1}{h_i}\frac{r_o}{r_i}\right)^{-1}$$

Where U is the overall heat transfer coefficient (W/m^2•K), h_o is the heat transfer coefficient on the outer fluid (W/m^2•K), h_i is the heat transfer coefficient on the inner fluid (W/m^2•K), r_o is the outer radius of the reactor tube (m), r_i is the inner radius of the reactor tube (m), and k is the thermal conductivity value of the reactor material (W/m •K)

In equation 40, a few assumptions were made to calculate U_o. The first and second terms were assumed to be close to 0 as h_o and k will be large values as they are the heat transfer coefficient of boiling water and the thermal conductivity of the piping. For the third term, r_o/r_i were assumed to be close to one, therefore U_o would be equal to h_i. An estimation of h_i was determined to be approximately 150 W/m^2 K as the fluid was treated as a dense fluid due to the packing of the catalyst (Peters, 1980). From all of this information, surface area, *A,* was then found to be 4554 m^2. To achieve this total surface area and the total reactor volume, a total of 676 tubes with 0.2 meter diameters are necessary.

The amount of boiling water needed to remove 68,303,400 W was then calculated through equation 41 below.

$$\text{(Eq. 41)} \qquad Q = \dot{m} \times \Delta H$$

where Q is the heat duty (W), ṁ is the molar flowrate (mol/s), and $\Delta H$is the heat of vaporization (J/mol)

The heat of vaporization was calculated at a temperature of 150 ℃, as that is the temperature of the boiling water that will act as the heat transfer fluid. The molar flowrate was calculated and converted to a volumetric flowrate of 109 m^3/hr.

Pressure Drop: The pressure drop for this reactor was also determined through use of the Ergun Equation, equation 36. The Ergun Equation shows that this reactor has a pressure drop of 0.3 bars, since this reactor is operating at 30.4 bars this pressure drop is insignificant to the design.

Catalyst Requirement Calculations: The catalyst requirement for this reactor was calculated using the GHSV value of the catalyst in the pilot plant, 12,000 (ml/g$_{\text{catalyst}}$ · hr), as well as the volumetric flowrate of the reactor. Using equation 37, the total amount of catalyst needed for this reactor was calculated to be 48254 kilograms by dividing the exhaust flowrate by the GHSV value of the catalyst.

Reactor Condenser Design

The purpose of condensers following the RWGS and Methanol synthesis reactors is to remove large amounts of water from the effluent streams of the reactors. Each condenser consists of one heat exchanger used to produce low pressure steam, a series of heat exchangers to lower the temperature of the stream, and a flash drum to separate the liquid and vapor streams. This method of lowering the temperature of the effluent reactor streams allows the plant to produce low pressure steam that can be used to heat other processes in other areas of the plant or sell the steam as steam credit.

Modeling Via Aspen Plus: Modeling of the condensers utilized three different types of blocks in Aspen: Heater, HeatX, and Flash2. The Heater and HeatX blocks were used in union; the Heater block was first simulated to calculate the required heat duty for the unit block, and the HeatX was then utilized to determine the flowrate of water/steam that was required. Similarly as previous simulations, all heat exchangers were modeled in ASPEN using the HeatX model. The *shortcut* calculation method was selected as the primary method of calculations, with all exchangers operating at a concurrent flow direction. The Flash2 blocks were used to determine the dimensions of the flash drum needed for desired separation of the vapor and liquid streams. This report will explore these condensers in further detail in the following sections.

Methanol Synthesis Condenser

The condenser following the methanol synthesis reactor is designed to condense the water and methanol from the vapor stream, which serves as a recycle stream back into the process. The liquid bottoms stream will then flow into a distillation column for methanol purification.

The first heat exchanger (E-802) in this condenser produces steam from boiler feed water at a rate of 2000 kmol/hr at 30℃ and 5 bars. The required surface area required for heat transfer was determined to be 195.8 m^2. To accommodate this surface area, E-802 requires a total of 674 tubes with the industry standard measurements. The cooling water will vaporize into steam, as 5 bars is under the saturation pressure at a steam outlet temperature of 160℃.

Next is a series of heat exchangers (E-803) to lower the temperature of the reactor effluent stream down to 35℃. The HeatX model determined that cooling water at an inlet temperature of 30℃ at a flow rate of 50000 kmol/hr would be sufficient to effectively lower the hot stream to the desired temperature. Similarly to the reverse water gas shift condenser, the surface area calculated for E-803 was determined to be 2910 m^2, which is greater than the recommended surface area for a single heat exchanger. Because of the large surface area required, there will be 3 shells in series with a total of 10010 tubes with the industry standard measurements.

The stream leaving the heat exchanger will flow into a flash drum (F-801). This flash drum will condense about 95% of the methanol to flow into the distillation column. The vapor will then be recycled into the RWGS reactor to utilize the unreacted gasses. The condenser design is summarized in **Figure 3.3.2-3**:

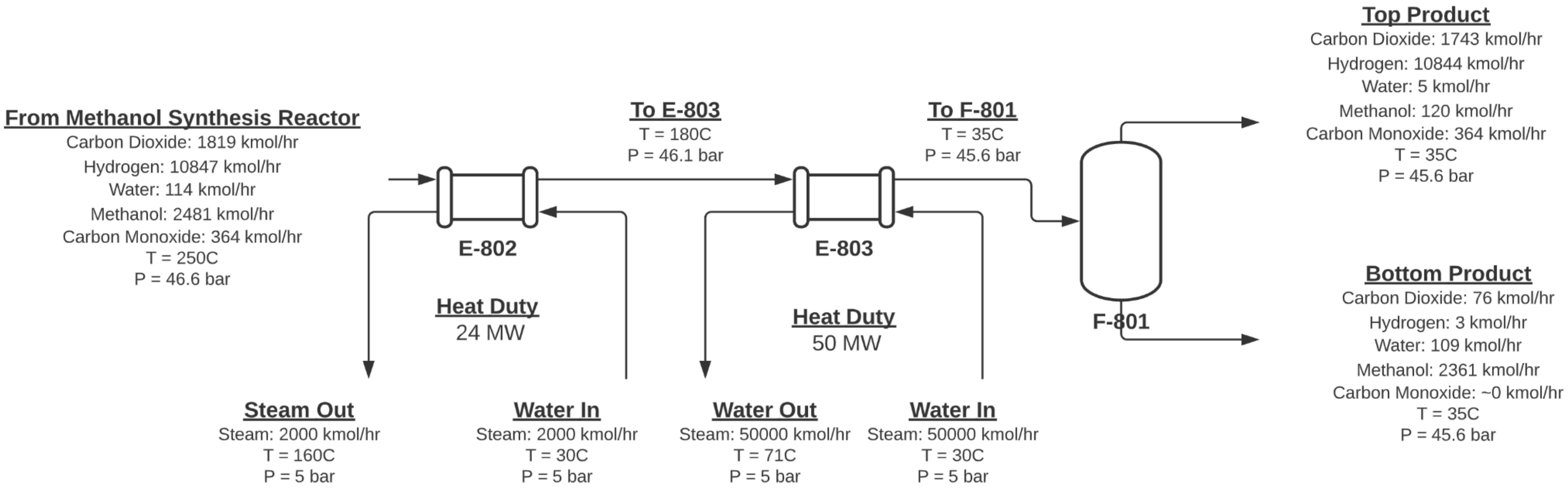


Figure 3.3.2-3 Schematic of the Methanol Condenser

3.3.3. Block 9: Distillation Tower

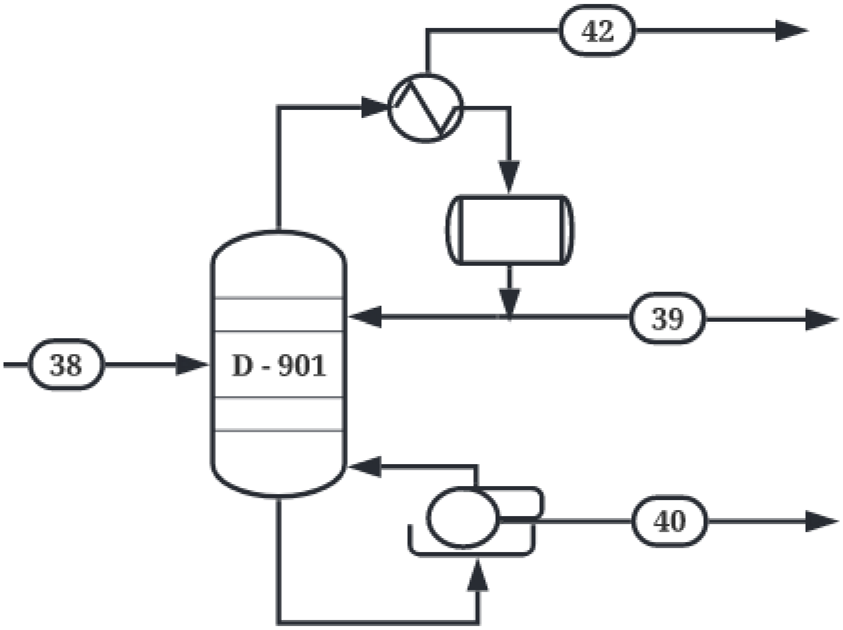


Figure 3.3.3-1 Block 9

Block 9 consists of the final distillation column in the system, which will be described below.

Distillation Tower Design

The purpose of the distillation column is to purify the final stream of methanol from water and residual gasses from the methanol reactor. A methanol purity of 98.5% was desired, as outlined by pilot plant data (Oh-Shim Joo, 1999). The operating pressure of the distillation column is 1 bar and the temperature of the incoming feed is 35℃, the operating temperature of the methanol condenser. Through Aspen Plus simulations, a purity of 99.6% was achieved in the product stream and a separation value of about 90% was reached, as shown in **Figure 3.3.3.2-1**.

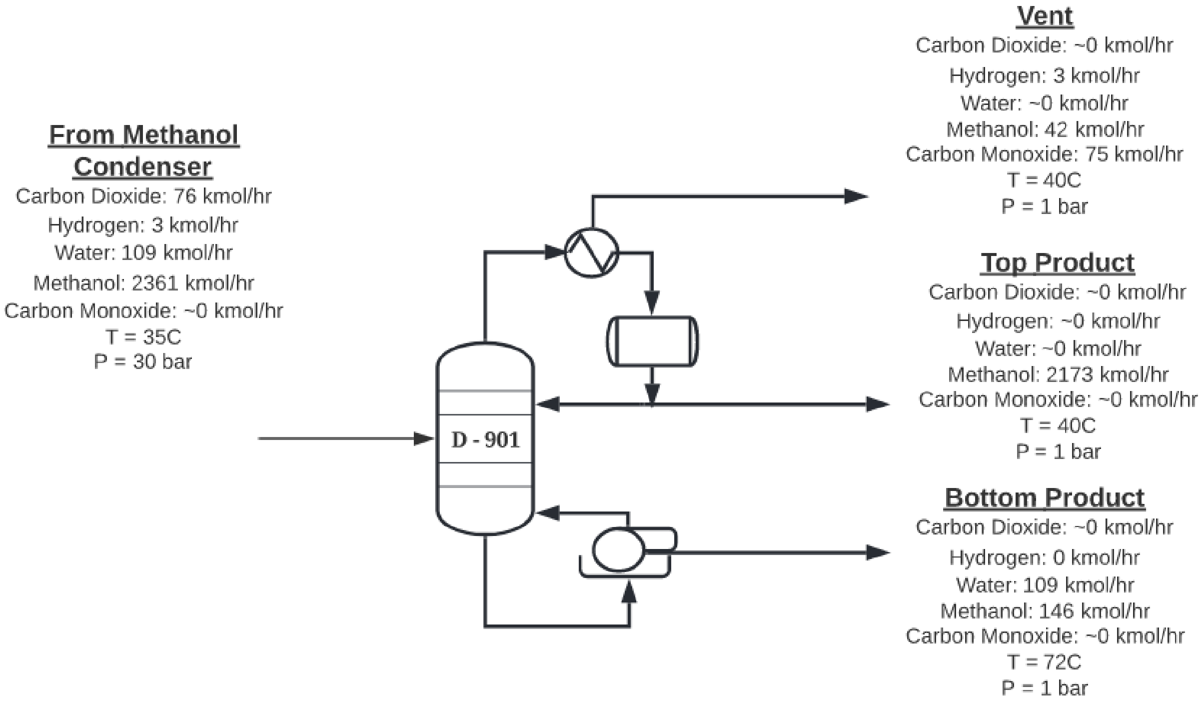


Figure 3.3.3-2 Schematic of the Distillation Column (D-901)

Modeling Via Aspen Plus: The distillation column was modeled through Aspen Plus using a RadFrac model as it is a more rigorous mode of calculation for systems with non-ideal components and multiple trays. Carbon dioxide, carbon monoxide, and hydrogen were specified as Henry Components to account for the solubility in the water stream in the column. A combination of the number of trays, reflux ratio, and distillate to feed ratio were optimized to maximize methanol purity in the product stream. First, a preliminary calculation of the minimum number of trays was computed using the Fenske Equation:

$$\text{(Eqn. 42)} \qquad N_{min} = \frac{ln(X_{D,LK}X_{B,HK}/X_{B,LK}X_{D,HK})}{ln\,\alpha_{LK,HK}} - 1$$

where N_{min} is the minimum number of stages, X_D is the distillate composition, X_B is the bottom composition, X_{LK} is the light key composition, X_{HK} is the heavy key composition, and $\alpha_{LK,HK}$ is the relative volatility.

Methanol and water acted as the light and heavy key respectively. From this equation, a minimum number of 10 trays was calculated. This value was set as a baseline in Aspen Plus and optimized throughout the distillation process. From this, it was found that 18 stages are the optimal number of trays to achieve separation. Per design heuristics and common industry standards, the tray height between each tray was simulated to be 0.61 meters. The reflux ratio and the distillate feed ratio were varied iteratively to produce to maximize methanol purity in the and produce flow rate. Multiple variations of reflux ratio and distillate to feed ratio were tested in

Aspen Plus, with optimal values selected to be 1.8 for the reflux ratio and 0.9 for the distillate to feed ratio. The feed stage was selected from an analysis of TPFQ data and state composition values. Out of the 18 total trays, tray 16 was selected as the feed tray as the methanol composition most closely matched the methanol feed composition. Through this simulation, the dimensions of the column were calculated by Aspen Plus. The column sizings and a summary of the operating conditions are tabulated in **Table 3.3.3-1**.

Table 3.3.3-1 Summary of Distillation Column Conditions and Dimensions

Stage	18
Feed Stage	16
Reflux Ratio	1.8
Distillate/Feed Ratio	0.9
Column Height (m)	14
Column Diameter (m)	6.2
Tray Height (m)	0.61
Condenser Heat Duty (MW)	67
Reboiler Heat Duty (MW)	68

A condenser is required for the distillation column and is designed to be a partial-vapor-liquid condenser as it will have both liquid and vapor streams. The liquid stream consists of an approximately pure methanol stream with a trace amount of carbon dioxide. The operating temperature of the condenser is 40℃ to fully condense the vapor. Cooling water will be needed for this unit, however, the amount of cooling water required to reach this temperature will be calculated in later works. As tabulated in **Table 3.3.3-1**, the heat duty required for the condenser is 67 MW. It will require a flow rate of approximately 231,512 kmol/hr of water and 5,255 m^2 of heat transfer area to condense the methanol. The remaining vapor out of the condenser comprises a small amount of carbon dioxide and methanol (31 kmol/hr and 17 kmol/hr respectively). Currently, the plan is to flare the vapor stream as a means to allow any impurities in the process to be removed.

The reboiler of the distillation column is a kettle reboiler and has an operating temperature of 72℃. From Figure 12, the bottom flow comprises only water and methanol, which was expected. However, the amount of methanol that is leaving the bottoms of the distillation column is not insignificant. Further economic analysis is required in order to determine if it is economically viable to lose 132 kmol/hr of methanol products or to install a subsequent separation unit, such as another distillation column, to this process. The heat duty required for the reboiler is 68 MW. This reboiler will require approximately 12,880 kmol/hr of steam and 152 m^2 of heat transfer area to properly function.

3.3.4. Methanol Synthesis Heat Exchanger Design

Reverse Water Gas Shift Heat Exchanger (E-701)

The first heat exchanger in the methanol synthesis system serves to heat the feed stream consisting of the product carbon dioxide from the DAC process as well as recycled carbon dioxide, carbon monoxide, and methanol to 500℃, the operating temperature of the first reactor. This will be a single pass countercurrent heat exchanger, with one current being the feed stream and the countercurrent being steam.

This unit operation was modeled using Aspen Plus, using the mixer and HeatX unit. The mixer unit was used to account for the combined feed and recycle flow entering the reactor. The HeatX unit was used due to its ability and versatility in calculating the necessary material and energy balances and because the heat exchanger's geometry was unknown. The *shortcut* calculation type of the unit was utilized. The *design* calculation type could then be used to find the surface area required for the necessary heat exchange. The input and output stream flow rates are outlined in **Figure 3.3.4-1.**

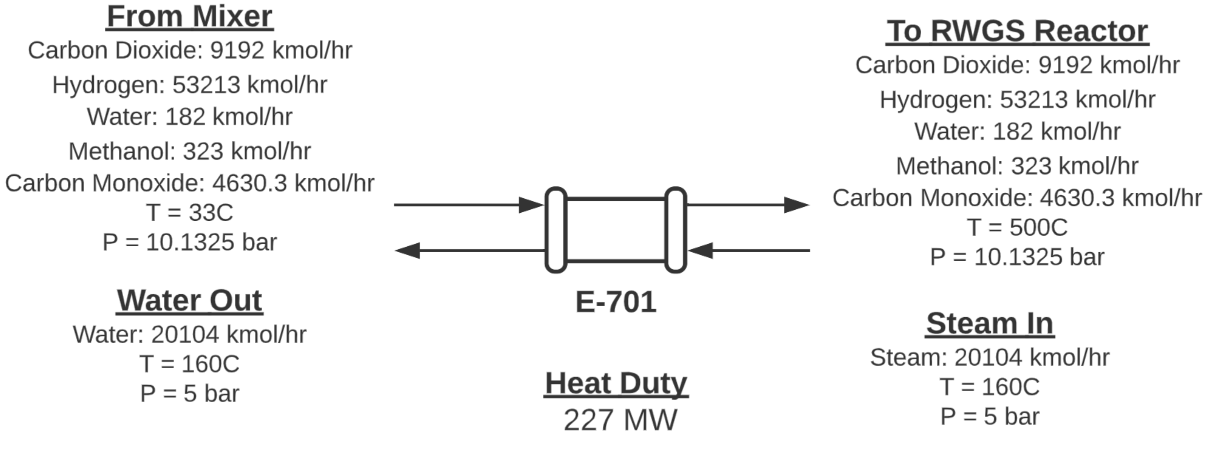


Figure 3.3.4-1 Schematic of Heat Exchanger (E-701)

Of note, the required surface area for E-701 was estimated through Aspen Plus to be 1865.5 m². According to design heuristics and current heat exchanger designs to account for this surface area two heat exchangers in series will be utilized with a tube length of 5 meters and outer diameter of 0.02 meters is recommended. 6,418 tubes are required in total for this series of heat exchangers and the tubes will be split across both heat exchangers. These heat exchangers will require a total of 20104 kmol/hr of steam to properly heat the stream to the temperature required for the reactor.

Methanol Synthesis Heat Exchanger (E-801)

This heat exchanger, just like the RWGS heat exchanger (E-701), is necessary to heat the feed stream of the methanol synthesis reactor up to the operating temperature of 250℃. Similarly to E-701, this unit operation was modeled in Aspen Plus using the mixer and HeatX units, and the design and shortcut calculation types. The input and output stream flow rates are outlined in **Figure 3.3.4-2**.

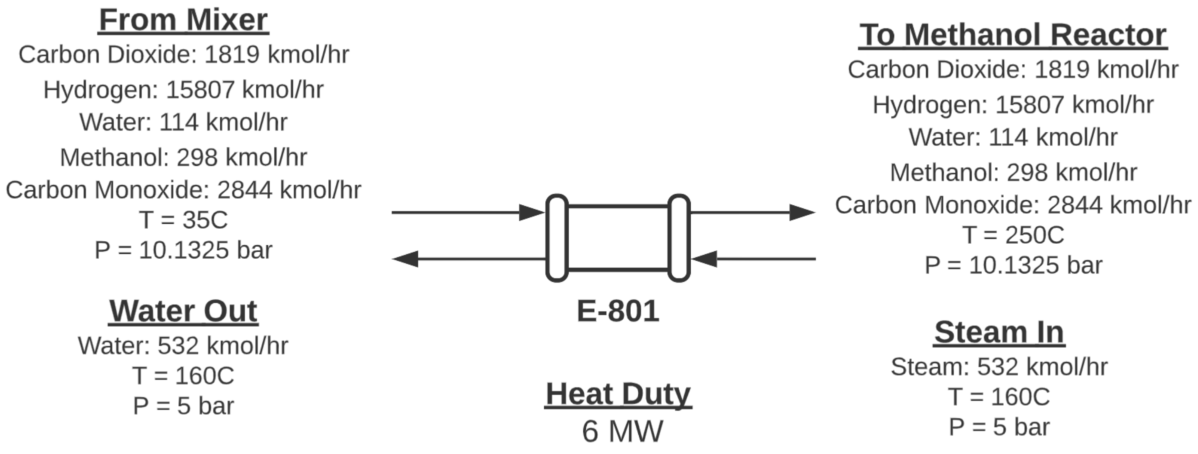


Figure 3.3.4-2 Schematic of Heat Exchanger 4 (E-801)

From simulations, it was found that the required surface area for sufficient heat transfer is 894.7 m², with 3078 tubes in total. A tube length of 5 m and outer diameter of 0.02 m was selected similarly to the design of E-701 in accordance with design heuristics and industry standards. This heat exchanger will require 532 kmol/hr of steam to heat the reactants to the proper temperature for the reactor.

3.3.5. Methanol Synthesis Process Stream Table

Table 3.3.5-2 Methanol Synthesis Overall Process Stream Table

Methanol Synthesis Process Stream Table

Stream #	CO_2	H_2	H_2O	CH_3OH	CO
29	4663.3	0.0	10.7	0.0	0.0
H1	0.0	13989.8	0.0	0.0	0.0
30	9326.5	31397.8	124.1	0.0	8704.0
31	4663.3	26734.5	4787.4	0.0	13367.2
32	0.0	0.0	4598.7	0.0	0.0
33	4663.3	26734.5	188.0	0.0	13367.2
34	2798.0	16040.7	112.8	0.0	8020.3
35	1865.3	10693.8	75.2	0.0	5346.9
36	1865.3	1367.3	75.2	0.0	683.6
37	1865.3	1367.3	0.6	0.0	683.6
38	0.0	0.0	74.6	4663.3	0.0
39	0.0	0.0	0.1	4263.7	0.0
40	0.0	0.0	74.5	399.2	0.0
41	4663.3	17408.0	113.4	0.0	8704.0
42	0.0	0.0	0.0	0.0	0.0

Related to the above stream stable, it should be known that various equipment sizing, design, and associated utility calculations in **Section 3.3** were conducted with a preliminary, inaccurate material balance, see **Table A.C-1**. Though, an accurate material balance was found and can be seen in the above table, **Table 3.3.5-2**. These corrected values are used for the revenue portion of the economic analysis.

While equipment in blocks 7, 8, and 9 should be redesigned with flowrates from **Table 3.3.5-2**, original design calculations and their associated utility and capital costs are conservative as flows and required feedstock are lower than originally expected. Therefore, the outlook of this project will improve once redesigns are made.

3.3.6 Compressor and Valve Design

Compressors:

In the methanol synthesis process compressors are utilized to compress gasses prior to their arrival to the appropriate reactor as well as to move vapor streams through the process. Two compressors were designed for this process C-801 and C-802. C-801 is located before the heat exchanger prior to the methanol synthesis reactor, R-801. This compressor promotes the flow of the RWGS reactor effluent as well as compresses it to the necessary pressure at 30.4 bar for the reaction in R-801. This stream primarily contains hydrogen gas as well as carbon monoxide, the reactants for the next reaction. This compressor requires 33.2 MW of power to adequately function.

The second compressor, C-802 is located after reactor R-801 and prior to the following condenser unit. This compressor pressurizes the reactor effluent stream slightly to 46.6 bar, the optimal temperature for methanol separation in the condenser unit. This pressure increase also accounts for the frictional losses through the piping and units of the condenser unit. It was designed in this manner to maximize the amount of product that would be obtained out of the process. This compressor requires 11.9 MW of power to run.

Valves:

One valve is utilized in the methanol synthesis process and it is located after the RWGS reactor, R-701. This valve is utilized to control the pressure of the reactor effluent stream into the condenser unit. While it is important to note that this valve is necessary, it is out of scope of this project to design the valve.

IV. ECONOMICS

4.1 Annual Revenue

The economic viability of this project is dependent on the anticipated annual revenue that is produced from the proposed air capture and methanol synthesis process. This process is aimed to produce approximately 819,654 metric tonnes of methanol annually. From Methanex Corporation, the current market price for methanol is $659 per metric tonne. Additionally, steam will be produced in the methanol synthesis process at a rate of 990,000 metric tonnes per year, which can be sold for a profit at 29 $/tonne, per industry standard (Turton, 2003). From these revenue sources, it is estimated that a total annual revenue of $570 million dollars will be collected. **Table 4.1-1** summarizes this information below.

Table 4.1-1 Anticipated Annual Revenue

Revenue	
Methanol Revenue	$540,151,780
Steam Revenue	$28,997,100
Annual Revenue	$569,148,880

4.2 Purchased Equipment and Capital Costs

In order to evaluate the economic viability of this project, the purchased equipment costs must be accounted for. These costs include the purchase of major equipment (reactors, vessels, mixers), heat exchangers, and pumps. The capital costs were calculated using CAPCOST, an excel program from Turton et al. **Table 4.2-1** summarizes the total capital costs for all pieces of equipment.

Table 4.2-1 Summary of Total Capital Costs

Total Capital Cost Summary

Tag	Total Cost	Lang Factor	Cost
Purchased Equipment Cost	$341,112,600	4.74	$1,616,873,724
Pump Equipment Cost	$70,124,400		$332,389,656
Heat Exchanger Cost	$15,858,500		$75,169,290
		Total Costs:	**$2,024,432,670**

4.2.1 Major Equipment

Major equipment such as reactor vessels, storage/pressure vessels, and mixers were all priced through CAPCOST. It was assumed that the reactors, storage vessels, and pressure vessels were designed with an maximum allowable stress of 944 bars and a weld efficiency of 0.9. This is summarized in **Table 4.2.1-1.**

Table 4.2.1-1 Summary of Purchased Equipment Cost

Purchased Equipment Cost Summary

Tag	Equipment Type	Equipment Costs	Number of Units	Cost
Block 1:				
R-101	Air Contactor	$114,200,000	1	$114,200,000
Block 2:				
R-201	Pellet Reactor	$76,900,000	1	$76,900,000
Block 3:				
R-301	Calciner	$10,804,800	1	$10,804,800
Block 4:				
R-401	Slaker	$33,000,000	1	$33,000,000
R-402	Slurry Mixer	$156,000	1	$156,000
Block 5:				
F-501	Flash drum	$325,000	1	$325,000
F-502	Flash drum	$258,000	1	$258,000
F-503	Flash drum	$214,000	1	$214,000
Block 6:				
Z-601	Power Island	$32,700,000	1	$32,700,000
Z-602	Steam Turbine	$6,700,000	1	$6,700,000
Z-603	Air Separation Unit	38,000,000	1	$38,000,000
Block 7:				
R-701	Reaction Vessel	$12,633,600	1	$12,633,600
F-701	Flash Drum	$3,389,200	1	$3,389,200
Block 8:				
R-901	Reaction Vessel	$9,504,000	1	$9,504,000
F-801	Flash Drum	$208,000	1	$208,000
Block 9:				
D-901	Distillation Column	$2,120,000	1	$2,120,000
			Total Costs:	$341,112,600

As mentioned, most of the costing was calculated via sizing or other relevant data in tandem with CAPCOST, “a Microsoft Excel macro-enabled file that allows the calculation of Equipment Costs, Total Plant Cost, Cost of Manufacturing (COMd), cash flow analysis, and Monte Carlo simulations of cash flows" (Richard, n.d.). However, some units did need additional sources to evaluate capital cost: the air contactor, pellet reactor, calciner, slaker, power island, steam turbine, and air separation unit.

Air Contactor, Pellet Reactor, Slacker, Power Island, Steam Turbine, Air Separation Unit:

First, the Air Contactor, Pellet Reactor, Slacker, Power Island, Steam Turbine, and Air Separation Unit will be described as costing for each of these units had the same source. The designed DAC plant is based off of Carbon Engineering’s design and economic analysis, and because these units are specific to direct air capture, equipment costing provided by carbon engineering was used. Of note, the calciner cost was not found from the Carbon Engineering report as a different unit was used in this project.

Calciner:

As mentioned previously in the report, sizing of the calciner is not possible. However, the equivalent heat duty was simulated via Aspen Plus, which allows for use of cost correlations. The cost correlation in figure **A.B-2**, see **Appendix B**, was used to find final equipment pricing.

4.2.2 Pumps Costs

This section will cover the equipment cost of pumps, conveyors, and compressors used in this process. The cost of pumps was determined using CAPCOST and inputs such as the necessary electric draw and the type of pump used. When a centrifugal pump is required, two units are set to be purchased to provide a backup pump in case of emergencies. Conveyor prices were determined using costing correlations between the conveying distance and purchasing cost using the mass flowrate of the solid being transferred (Peters & Timmerhaus, 1980), see **Figure A.B.2** in **Appendix B**. Cost of the compressors were found using CAPCOST based on ASPEN simulated power requirement. The equipment costs of all pumps, conveyors, and compressors are listed in **Table 4.2.2-1** below.

Table 4.2.2-1 Summary of Pump Cost

Purchased Pump Cost Summary

Tag	Equipment Type	Equipment Costs	Number of Units	Cost
P-101	Centrifugal	$91,200	2	$182,400
P-102	Centrifugal	$179,000	2	$358,000
P-403	Centrifugal	$157,000	2	$314,000
P-201	Conveyor	$450,000	1	$450,000
P-301	Conveyor	$450,000	1	$450,000
P-302	Conveyor	$450,000	1	$450,000
P-303	Conveyor	$320,000	1	$320,000
P-402	Conveyor	$320,000	1	$320,000
C-501	Centrifugal	$10,000,000	1	$10,000,000
C-502	Centrifugal	$4,970,000	1	$4,970,000
C-503	Centrifugal	$3,010,000	1	$3,010,000
C-801	Centrifugal	$36,500,000	1	$36,500,000
C-802	Centrifugal	$12,800,000	1	$12,800,000
			Total Costs:	$70,124,400

4.2.3 Heat Exchangers Costs

This section will discuss the purchasing costs of heat exchangers used in the designed process to include furnace heaters, cyclone heat exchangers, coolers, and shell and tube heat exchanger. The costs of the furnace heater and coolers were found using CAPCOST based on heat duties from ASPEN simulations. The cyclone heat exchangers were also found via CAPCOST based on volumetric flowrate of the vapor phase, as determined from material balances. The shell and tube heat exchangers were also simulated in ASPEN to determine the surface area required for heat transfer and input into CAPCOST for its associated purchasing cost.

Table 4.2.3-1 Summary of Heat Exchanger Costs

Purchased Heat Exchanger Cost Summary

Tag	Equipment Type	Equipment Costs	Number of Units	Cost
E-201	Furnace Heater	$2,390,000	1	$2,390,000
E-301	Cyclone Heat Exchanger	$70,700	1	$70,700
E-302	Cyclone Heat Exchanger	$70,700	1	$70,700
E-303	Cyclone Heat Exchanger	$31,300	1	$31,300
E-501	Cooler	$2,110,000	1	$2,110,000
E-502	Cooler	$1,410,000	1	$1,410,000
E-503	Cooler	$403,000	1	$403,000
E-701	Shell/Tube Heat Exchanger	$1,170,000	1	$1,170,000
E-702	Shell/Tube Heat Exchanger	$725,000	1	$725,000
E-703	Shell/Tube Heat Exchanger	$5,340,000	1	$5,340,000
E-801	Shell/Tube Heat Exchanger	$19,800	1	$19,800
E-802	Shell/Tube Heat Exchanger	$178,000	1	$178,000
E-803	Shell/Tube Heat Exchanger	$1,940,000	1	$1,940,000
			Total Costs:	$15,858,500

4.2.4 Total Capital Costs of Plant

The total capital cost of the plant was approximated using the Lang Factor equation. This equation describes the calculation of the total capital costs of a plant, by multiplying the total equipment cost by a Lang Factor value. The Lang Factor estimation includes other costs associated with plant costs, such as installation, plumping, controls, and land. In this approximation, a value of 4.74 was used for the Lang Factor. The total capital cost estimate was found to be $2,074,711,718. The Lang Factor Equation is described below and the total capital cost is found in **Table 4.2-1.**

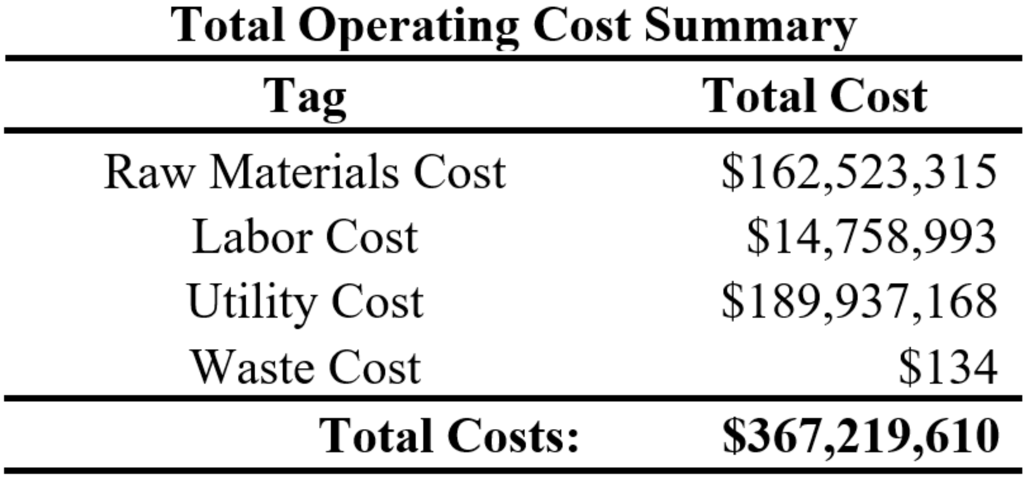
$$\text{(Eq. 43)} \qquad C_{TM} = (F_{Lang}) \sum C_{E,i}$$

where C_{TM} is the total capital cost of the plant, F_{Lang} is the lang factor, , and $\sum C_{E,i}$ is the capital cost of the plant.

4.3 Operating Costs

The Operating Costs of the plan consists of four individual costs: raw materials, labor costs, utility cost, and wastes costs. The prices for each section are summarized in **Table 4.3.1-1** below. The largest price component from the total cost are the utility costs, as the heat exchangers in our processes require large amounts of electricity and steam/cooling water for the large differences in temperature and pressures between streams.

Table 4.3.1-1 Summary of Raw Materials Cost



Total Operating Cost Summary

Tag	Total Cost
Raw Materials Cost	$162,523,315
Labor Cost	$14,758,993
Utility Cost	$189,937,168
Waste Cost	$134
Total Costs:	**$367,219,610**

4.3.1 Raw Materials

The cost per unit for the two catalysts, ZnO/Al_2O_3 and $Cu/ZnO/Al_2O_3$ were found through Alibaba Resources in 2021. The price of hydrogen was found through current price estimates of Blue Hydrogen by KPMG, SPGlobal, and GaffneyCline (Powell, 2020). The price of $Ca(OH)_2$, CH_4, KOH were found from US Energy Information Administration and Made-In-China Suppliers. The information is summarized below in **Table 4.3.1-1.**

Table 4.3.1-1 Summary of Raw Materials Cost

Raw Materials Cost Summary

Component	Amount Required/a	Unit/a	Cost per Unit	Cost
ZnO/Al_2O_3	74027	Kg	$15.00	$1,110,405
$Cu/ZnO/Al_2O_3$	48254	Kg	$12.00	$579,048
Hydrogen	51816667	Kg	$2.50	$129,541,667
$Ca(OH)_2$	271333	Kg	$0.40	$108,533
KOH	419796	Kg	$0.74	$308,550
CH_4	5145852000	Thousand Ft^3	$6.00	$30,875,112
			Total Costs:	**$162,523,315**

4.3.2 Labor Costs

In order to find the necessary number of operators to hire and have on shift at all times, equation 44 from the Turton textbook was used (Turton, 2003).

$$\text{(Eq. 44)} \quad N_{ol} = (6.29 + 31.7P^2 + 0.23N_{mp})^2$$

Where N_{ol} is the number of operators per shift, P is the number of operating steps that handle particulate solids, and N_{mp} is the number of major pieces of equipment

Using this equation, the total labor costs using the average salary of a chemical plant operator was found in **Table 4.3.2-1.** The highlighted equipments represent all equipment that qualify as P variables, and the rest are N_{mp} variables. Overall, almost \$15 million will be spent in labor each year in order to keep the plant in operation.

Table 4.3.2-1 Summary of Labor Costs

Operating Labor Cost Summary

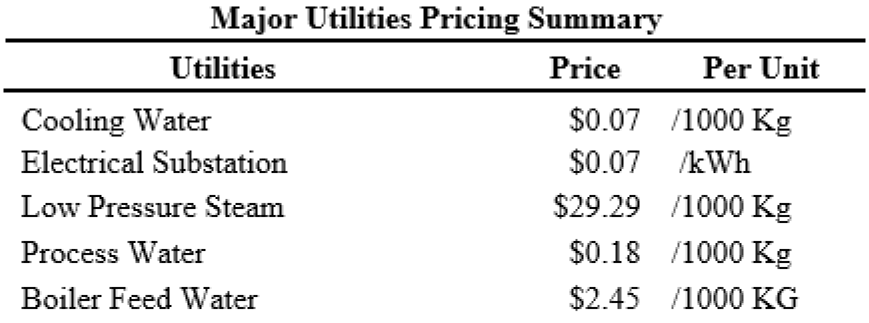
Block	Equipment Type	Nnp	Nol	Operators Required
Block 1:				
R-101	Air Contactor	3	2.64	12
P-101	K2CO3 Pump			
P-102	KOH Pump			
Block 2:				
R-201	Pellet Reactor	3	6.22	28
P-201	Conveyor			
E-201	Heater			
Block 3:				
R-301	Calciner	4	17.10	77
P-301	Conveyor			
P-302	Conveyor			
P-303	Conveyor			
E-301	Cyclone Heat Exchanger			
E-302	Cyclone Heat Exchanger			
E-303	Cyclone Heat Exchanger			
Block 4:				
R-401	Slaker	3	11.57	53
R-402	Slurry Mixer			
P-401	Conveyor			
P-402	Conveyor			
P-403	Pump			
Block 5:				
C-501	Centrifugal Compressor	9	2.89	14
C-502	Centrifugal Compressor			
C-503	Centrifugal Compressor			
E-501	Cooler			
E-502	Cooler			
E-503	Cooler			
F-501	Flash drum			
F-502	Flash drum			
F-503	Flash drum			

Block 6:				
Z-601	Power Island	3	2.64	12
Z-602	Steam Turbine			
Z-603	Air Separation Unit			
Block 7:				
R-701	Reaction Vessel	5	2.73	13
F-701	Flash Drum			
E-701	Shell/Tube Heat Exchanger			
E-702	Shell/Tube Heat Exchanger			
E-703	Shell/Tube Heat Exchanger			
Block 8:				
R-801	Reaction Vessel	7	2.81	13
F-801	Flash Drum			
C-801	Centrifugal Compressor			
C-802	Centrifugal Compressor			
E-801	Shell/Tube Heat Exchanger			
E-802	Shell/Tube Heat Exchanger			
E-803	Shell/Tube Heat Exchanger			
Block 9:				
D-901	Distillation Column	3	0.83	4
		Total Operators Required:		225
		Base Salary Annually:		$65,460
		Total Labor Cost Annually:		$14,758,993

4.3.3 Utility Costs

The utilities necessary for this designed process include electrical power, process water, and steam. The price of each utility is shown below in **Table 4.3.3-1.**

Table 4.3.3-1 Summary of Utilities Pricing



Major Utilities Pricing Summary

Utilities	Price	Per Unit
Cooling Water	$0.07	/1000 Kg
Electrical Substation	$0.07	/kWh
Low Pressure Steam	$29.29	/1000 Kg
Process Water	$0.18	/1000 Kg
Boiler Feed Water	$2.45	/1000 KG

The utility price associated with each block of the designed process is shown in **table 4.3.3-2.** This outlines the utility required, quantity required, and the associated cost. The overall process will require approximately $189 million per year for utilities alone.

Table 4.3.3-2 Summary of Utilities Cost

Utility Cost Summary				
Block	**Equipment Type**	**Amount/a**	**Units**	**Cost**
Block 1:				
R-101	Air Contactor Power	80,360,000	kWh	$5,416,264
P-101	K2CO3 Pump Power	480,000	kWh	$32,352
P-102	KOH Pump Power	1,746,000	kWh	$117,680
			Block 1 Total Annual Cost:	**$5,566,296**
Block 2:				
R-201	Pellet Reactor Power	26,460,000	kWh	$1,783,404
P-201	Conveyor Power	2,421,000	kWh	$163,175
E-201	Heater Power	138,000,000	kWh	$9,301,200
			Block 2 Total Annual Cost:	**$11,247,779**
Block 3:				
R-301	Calciner Oxygen Flow Power	91,072,000	kWh	$6,138,253
P-301	Conveyor Power	2,421,957	kWh	$163,240
P-302	Conveyor Power	2,421,957	kWh	$163,240
P-303	Conveyor Power	2,421,957	kWh	$163,240
E-301	Cyclone Heat Exchanger Power	100,200,000	kWh	$6,753,480
E-302	Cyclone Heat Exchanger Power	139,200,000	kWh	$9,382,080
E-303	Cyclone Heat Exchanger Power	22,800,000	kWh	$1,536,720
			Block 3 Total Annual Cost:	**$24,300,253**
Block 4:				
R-401	Slaker	66,073,393	kWh	$4,453,347
R-402	Slurry Mixer Power	2,418,000	kWh	$162,973
	Process Water	1,885,040,420	Kg	$339,307
P-401	Conveyor Power	202,904	kWh	$13,676
P-402	Conveyor Power	2,853,785	kWh	$192,345
P-403	Pump Power	1,056,000	kWh	$71,174
			Block 4 Total Annual Cost:	**$5,232,822**
Block 5:				
C-501	Compressor Power	164,880,000	kWh	$11,112,912
C-502	Compressor Power	80,562,000	kWh	$5,429,879
C-503	Compressor Power	49,056,000	kWh	$3,306,374
E-501	Cooler Water	18,812,730,401	Kg	$1,260,453
E-502	Cooler Water	12,566,843,568	Kg	$841,979
E-503	Cooler Water	3,199,712,040	Kg	$214,381
			Block 5 Total Annual Cost:	**$22,165,977**

Block 7:				
R-701	Reactor (Steam for Heat Required)	550,574,170	Kg	$16,126,317
E-701	Shell/Tube Heat Exchanger Steam	2,173,644,480	Kg	$63,666,047
E-702*	Shell/Tube Heat Exchanger Water	345,600,000	Kg	$846,720
E-703	Shell/Tube Heat Exchanger Water	1,555,200,000	Kg	$104,198
			Block 7 Total Annual Cost:	**$80,743,283**
Block 8:				
R-801*	Reactor (Water for Heat Removal)	414,000,000	Kg	$1,014,300
C-801	Centrifugal Compressor Power	198,960,000	kWh	$13,409,904
C-802	Centrifugal Compressor Power	71,388,000	kWh	$4,811,551
E-801	Shell/Tube Heat Exchanger Steam	57,519,840	Kg	$1,684,756
E-802*	Shell/Tube Heat Exchanger Water	230,400,000	Kg	$564,480
E-803	Shell/Tube Heat Exchanger Water	480,000,000	Kg	$32,160
			Block 8 Total Annual Cost:	**$21,517,151**
Block 9:				
D-901	Condenser Power	643,200,000	Kg	$43,094
	Reboiler Power	652,800,000	Kg	$19,120,512
			Block 9 Total Annual Cost:	**$19,163,606**
			Total Costs:	**$189,937,168**

Equipment marked with * indicates that steam is produced and associated costs will be gained as revenue through steam credits.

4.3.4 Waste Costs

The amount of waste generated from the proposed process is low. The only meaningful waste stream from the DAC process is a gas purge that ultimately has no consequence when vented back into the atmosphere. As for the methanol production, the main waste streams are stream 32 and 41; the condensed liquids from the RWGS condenser, and the bottoms product of the distillation tower respectively. Both these streams of wastewater need to be treated before being released back into sewage or other appropriate water storage methods safely. The cost of the wastewater treatment was taken from Turton table 8.3 and used to calculate how much it will be to treat all of the wastewater streams in the plant (Turton, 2003).

Table 4.3.3-1 Summary of Waste Cost

Waste Stream Cost

Stream	Waste Stream	Amount (m^3/a)	Total Cost
34	Waste Water from RWGS Condenser	2,294	$128
42	Waste Water from Distillation	105	$6
		Total:	$134

4.4 Cost of Manufacturing

The “Cost of Manufacturing” value can be broken down into three categories, direct costs, fixed costs, and general manufacturing costs. Direct costs relate to the rate of production of the final product, fixed costs represent items that have no dependence with the rate of production and general manufacturing costs are items that relate to administrative and development costs. These values were calculated from equations described in Turton et al. **Table 4.4-1** summarizes the calculated costs for this process.

Table 4.4-1 Summary of Manufacturing Cost

Manufacturing Cost Summary

Category	Estimation	Annual Cost (Thousands of Dollars)
Direct Costs:		
Raw Materials	CRM	$162,523
Operating Labor Cost	COL	$14,759
Utilities Cost	CUT	$189,937
Direct Supervisory and Clerical Labor	0.18COL	$2,657
Maintenance and Repairs	0.06FCI	$121,466
Operating Supplies	0.009FCI	$18,220
Laboratory Charges	0.15COL	$2,214
Patents and Royalties	0.03COM	$25,212
Fixed Costs:		
Depreciation	0.1FCI	$202,443
Local Taxes and Insurance	0.032FCI	$64,782
Plant Overhead Costs	0.708COL + 0.036FCI	$83,329
General Manufacturing Costs:		
Administration Costs	0.177COL + 0.009FCI	$20,832
Distribution and Selling Costs	0.11COM	$92,443
Research and Development	0.05COM	$42,020
	Total Costs (COM):	$840,394
	Total Costs + Depreciation:	$1,042,837

The working capital is the additional cost required to smoothly run plant operations during the first year of plant operations. The additional investments of funds covers initial raw material purchase, labor costs, and possible equipment errors. Turton et al. defines the working capital as approximately 15% of the fixed capital investment (FCI). The calculation is summarized in **Table 4.4-2.**

Table 4.4-2 Summary of Total Capital Costs

Total Capital Cost Summary		Annual Cost (Thousands of Dollars)
Fixed Capital Investment	FCI	$2,024,433
Working Capital Investment	0.15FCI	$303,665
Total Capital Cost Summary	FCI + 0.15FCI	$2,328,098

4.5 Cash Flow Analysis

For this analysis, a standard tax rate of 30% was applied for any gross profit annually. A 10-year straight line depreciation was incorporated into this analysis, with an annual depreciation rate of $202,443,267. A 20 year plant operation was assumed, and for each year, the cumulative cash position, discount factor, and the present value of the cash flow was calculated. This is summarized **Table 4.5-1 and Figure 4.5-1.**

Table 4.5-1 Summary of Cumulative Cash Position Values.

Year	Net after-tax cash flow (Million USD)	Cumulative Cash Position	Discount Factor	Present Value of Cash Flow
-2	-$1,012	-$1,012.22	1.029765661	-1042.35
-1	-$2,024	-$3,036.65	1.014773699	-2054.34
0	-$386	-$3,422.96	1	-386.31
1	$202	-$3,221.03	0.985441385	198.99
2	$202	-$3,019.10	0.971094724	196.09
3	$202	-$2,817.17	0.95695693	193.24
4	$202	-$2,615.24	0.943024963	190.42
5	$202	-$2,413.31	0.929295826	187.65
6	$202	-$2,211.38	0.915766566	184.92
7	$202	-$2,009.45	0.902434273	182.23
8	$202	-$1,807.52	0.889296081	179.57
9	$202	-$1,605.60	0.876349162	176.96
10	$202	-$1,403.67	0.863590732	174.38
11	$143	-$1,260.82	0.851018047	121.57
12	$141	-$1,119.47	0.838628403	118.54
13	$141	-$978.11	0.826419135	116.81
14	$141	-$836.76	0.814387618	115.11
15	$141	-$695.41	0.802531262	113.44
16	$141	-$554.06	0.790847519	111.79
17	$141	-$412.71	0.779333875	110.16
18	$141	-$271.36	0.767987853	108.56
19	$141	-$130.01	0.756807014	106.98
20	$800	$670.29	0.745788952	596.86

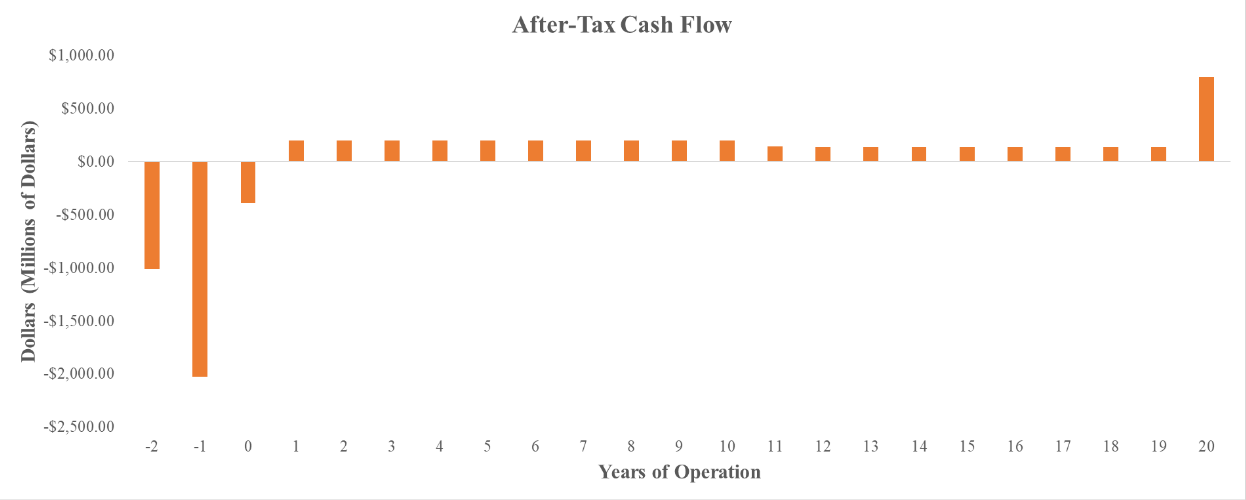


Figure 4.5-1 After-Tax Cash Flow Analysis

The After-Tax Cash Flow analysis from **Figure 4.5-1** estimates that this process will continuously lose revenue over the 20 years the plant is in operation. The profitability of the project can be further explored by calculating the internal rate of return (IRR), which was calculated to be 1.47%. This would signal that this process is not a worthy investment, as the investor would not make a large return investment on the initial capital invested.

4.6 Scenarios

From previous discussion, it can be seen that this project lacks economic viability. However, there are a few factors that can be considered which have the potential to improve the economic outlook of the project. Two scenarios are evaluated in the following section to understand how to improve the feasibility of this DAC to methanol synthesis process.

Scenario 1: Carbon Credits

One marketable aspect of this project is that it is centered around direct air capture; meaning that this manufacturing process intakes carbon dioxide instead of producing it and gives the opportunity to sell carbon credits. Carbon credits are a tradeable certificate that allows an individual with the credit the right to emit one tonne of carbon dioxide. The goal of carbon credits is to give manufacturers accountability in terms of their greenhouse gas emissions.

Mandates on carbon credits will cause an incentive for some companies to purchase carbon credits so that they can emit more. However, processes that offset carbon emissions can accumulate a surplus of carbon credits, therefore the ability to sell the credits to subsidize the project (Carbon Credit, 2021). While there is variability in market processes due to supply and demand and other factors, the cost of carbon credits is reported to be between 40-80$/tonne of carbon. This scenario assumes a sale of 80$/tonne of carbon extracted from the atmosphere.

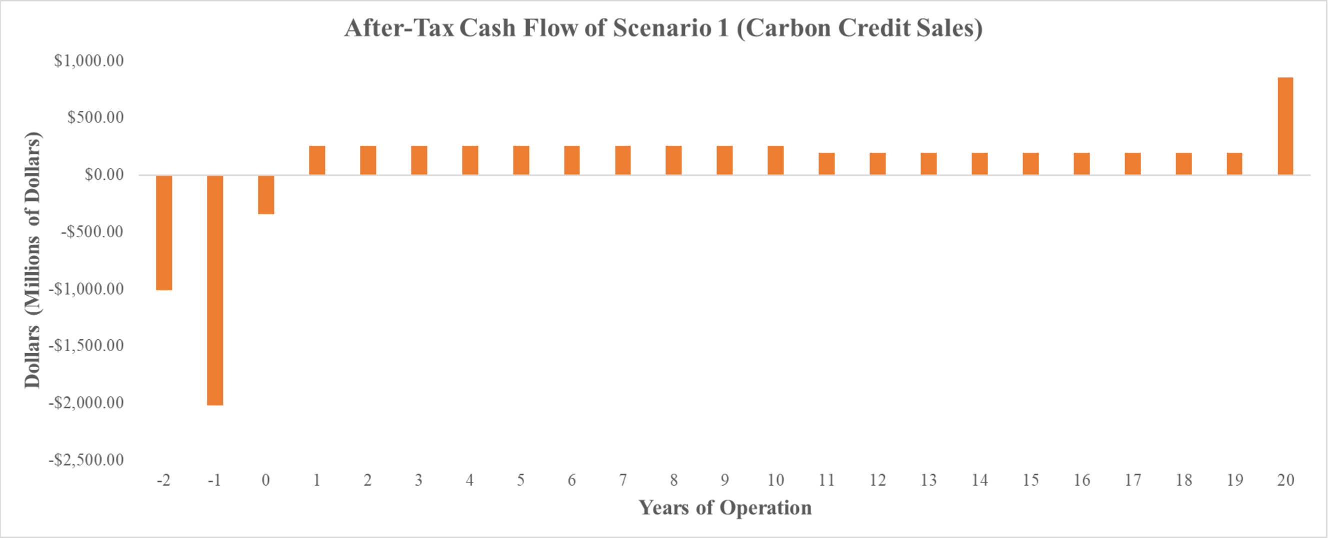


Figure 4.6-1 After-Tax Cash Flow Analysis Representation Scenario 1

From **Figure 4.6-1**, it can be seen that carbon credits are not enough to improve the economic viability of DAC such that it is sufficiently profitable. With a resulting IRR of 3.7%, other options should also be considered to improve profitability.

Scenario 2: Premium Methanol

As many entities will be incentivised to make sustainable decisions, a premium can be put on the methanol produced from direct air capture. Reports show that sustainable methanol can be sold at prices as high as 2400$/tonne (Greenhaleg, 2021).

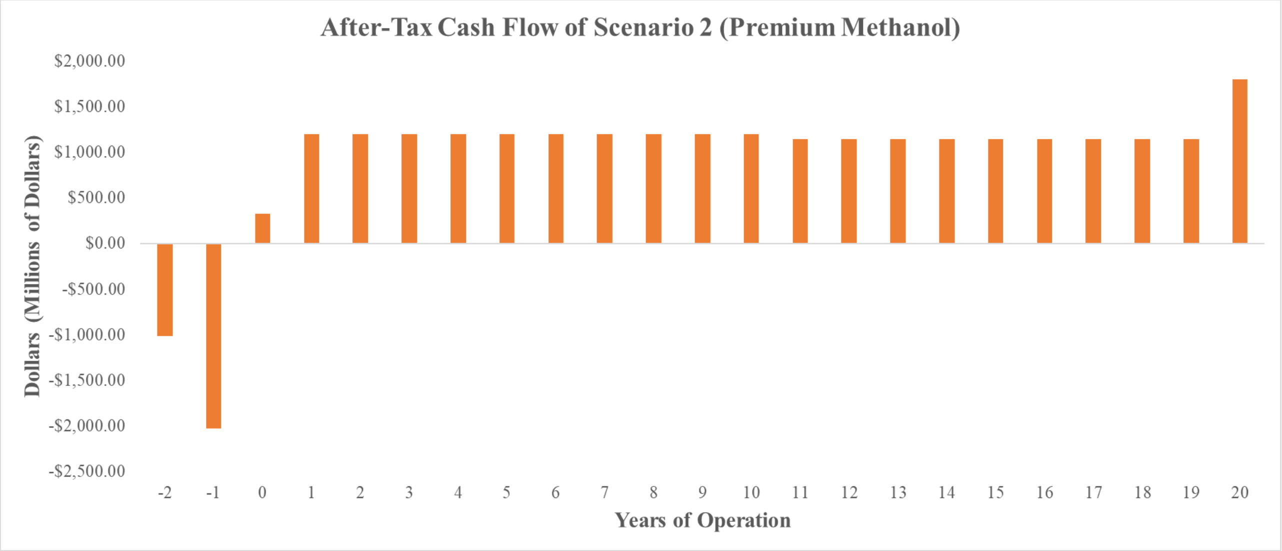


Figure 4.6-2 After-Tax Cash Flow Analysis Representation Scenario 2

From **Figure 4.6-2**, it can be seen that selling methanol at a premium rate allows for this project to become highly profitable. With an IRR at 29.8%, this scenario would enable the ability for DAC to methanol synthesis to be a worthy investment.

4.7. Overall Project Economics Outlook and Profitable Suggestions

Methanol produced by traditional petroleum plants can be sold at low rates due to relatively low capital and operating costs associated with methanol synthesis via syngas. This strategy is an industry standard and uses a waste component of a profitable manufacturing process, making profitability easy. Therefore, the competitive market makes it difficult for the DAC to methanol synthesis plant to be lucrative. To this end, under the current economic outlook of this plant, construction cannot be recommended despite a positive cashflow. While this project projects an IRR percentage of 1.47%, this is still below the recommended project viability value of 10% and therefore cannot be greenlit.

V. ENVIRONMENTAL CONSIDERATIONS

5.1. Direct Air Capture

As mentioned previously in this report, to achieve the goals outlined in the Paris Climate Agreements, direct air capture technologies can play a crucial role. The process that has been designed in this report will have a dominant beneficial impact on the environment as it will capture a total of 0.97 Mt-CO_2/year from the atmosphere.

This section will also discuss the potential environmental impact of the direct air capture units to include the air contactor, pellet reactor, calciner, and slaker. The air contactor is one of the largest points of potential environmental impact. The air contactor is based off of forced-draught cooling tower technology, as such "drift" could potentially be an issue. Drift is ingested debris and droplets that may then be released into the environment. This drift could mean release of droplets of the aqueous sorbent, potassium hydroxide. To manage this, drift eliminators can be installed. This unit is not fully designed in this report, so further elaboration on drift eliminators will not be provided. Though, reference economic evaluations of the unit do include the addition of this equipment.

For the pellet reactor, it is essential to consider that the reactor itself houses chemicals that are reported to be potentially hazardous to health, corrosive to metals, and harmful to aquatic life. All materials should remain in the system and units will be designed to deter corrosion.

When considering the environmental impacts of the calciner, the most notable risk assessed is related to the amount of heat that the calciner requires. Heat pollution can have devastating effects on natural wildlife, changing the way animals behave and also having an impact on the flora of an area. Though, this unit is designed to be adiabatic and heat created in the unit must be retained in order for the target reactions to occur. The slaker also requires high temperatures with high pressure steam, so its environmental considerations are similar to that of the calciner's.

Direct Air Capture Waste Streams

The main source of waste from the Direct Air Capture portion of this plant is found in stream 5, the Pellet Reactor Gas Purge. This stream contains very minimal amounts of carbon dioxide, oxygen, and nitrogen. The quantity of purge gas is insignificant and any venting into the atmosphere will have little to no consequences on the environment, especially when considering the amount of carbon dioxide that is taken out of the atmosphere through our process.

5.2 Methanol Synthesis

Methanol Synthesis Waste Streams

The only evaluated environmental risk associated with methanol synthesis is waste. The main waste that is produced from the reverse water gas shift reactor is unreacted carbon dioxide as well as water. Fortunately, the waste carbon dioxide is recycled to extinction in this process, and the only component of any waste streams (streams 32 and 41) is water and trace amounts of methanol. The wastewater streams are treated before being drained back out to sewage any other appropriate waste water collection. A biodegradation process can be used to treat the methanol out of the wastewater stream so that it is safe to dispose of (Boudemagh, 2006). Because of the recycle to extinction stream in this project design, this is the only waste stream in the methanol synthesis side of the process that will have any effects on the environment.

VI. SAFETY CONSIDERATIONS

6.1. Chemical Hazards and Compatibility

6.1.1. DAC Chemical Hazards and Compatibility

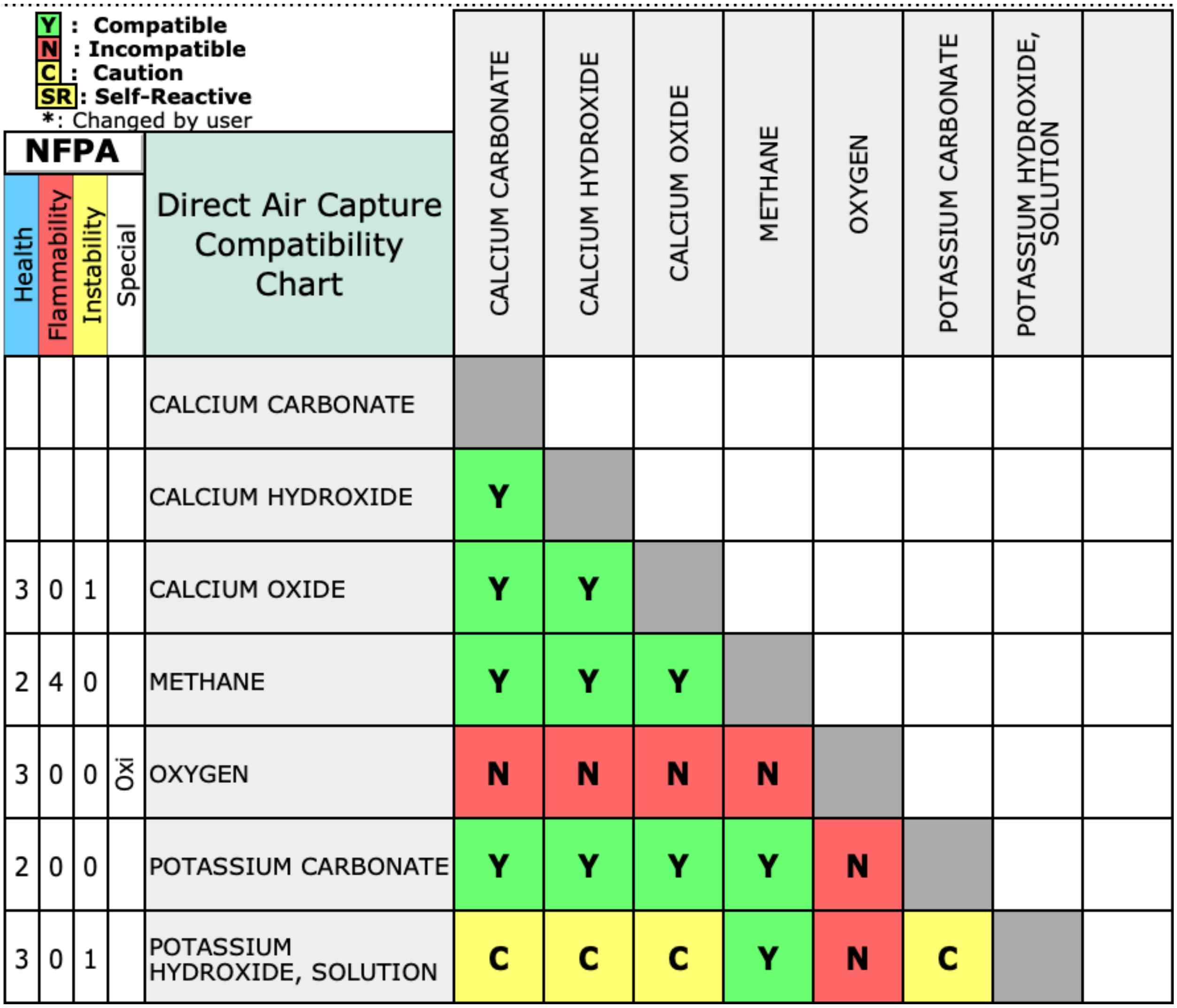
Many of the chemicals used in this process can cause serious health effects from both short term and long term exposure. These hazards must be identified and proper procedures must be put in place in order to mitigate any risks or potential accidents from occuring. Moreover, the compatibility of the chemicals involved must be analyzed so that unwanted reactions can be prevented should chemicals be exposed to each other in an uncontrolled environment. Considering the DAC process, calcium carbonate, calcium hydroxide, calcium oxide, potassium carbonate, and potassium hydroxide are chemicals of note.

Calcium carbonate can cause skin and eye irritation from short term exposure. When inhaled, coughing and nose irritation can occur. While these short term health effects can be harmful, generally there are no signs of long term exposure health effects. The same cannot be said for calcium hydroxide; short term exposure can seriously irritate, or even burn, the skin and eyes and cause lasting damage. Inhalation of calcium hydroxide can not only irritate the nose, throat and lungs, but can cause coughing or breathing complications. Calcium oxide shares the same adverse short term health effects as calcium hydroxide but can also cause fluid build up in the lungs, or pulmonary edema, when exposed to higher concentrations of the chemical. Long term exposure to calcium oxide can cause skin and nail damage. With these harmful health effects in mind, it is important for not only the operators to be wearing proper personal protective equipment, but that the equipment housing these chemicals, like the calciner or pellet reactor, are properly and regularly maintenanced so that any potential leaks or spills do not occur.

The other two chemicals, potassium carbonate and potassium hydroxide, also both cause serious eye and skin irritation and have the potential to cause burns. Potassium hydroxide can also cause a pulmonary edema if exposed to higher concentrations, similar to calcium hydroxide. Potassium hydroxide poses a long term risk of developing skin allergies and chronic bronchitis.

Potassium carbonate poses a different risk from its hydroxide counterpart, it is extremely harmful to aquatic life as it increases the pH of waterways. Similar to the necessary prevention steps for all the calcium chemicals, proper PPE and routine maintenance of the equipment housing these chemicals is absolutely crucial to ensure that any spills or leaks are prevented from occurring.

Table 6.1-1 Chemical Compatibility Chart for Direct Air Capture



Y : Compatible
N : Incompatible
C : Caution
SR : Self-Reactive
*: Changed by user

NFPA												
Health	Flammability	Instability	Special	Direct Air Capture Compatibility Chart	CALCIUM CARBONATE	CALCIUM HYDROXIDE	CALCIUM OXIDE	METHANE	OXYGEN	POTASSIUM CARBONATE	POTASSIUM HYDROXIDE, SOLUTION	
				CALCIUM CARBONATE								
				CALCIUM HYDROXIDE	Y							
3	0	1		CALCIUM OXIDE	Y	Y						
2	4	0		METHANE	Y	Y	Y					
3	0	0	Oxi	OXYGEN	N	N	N	N				
2	0	0		POTASSIUM CARBONATE	Y	Y	Y	Y	N			
3	0	1		POTASSIUM HYDROXIDE, SOLUTION	C	C	C	Y	N	C		

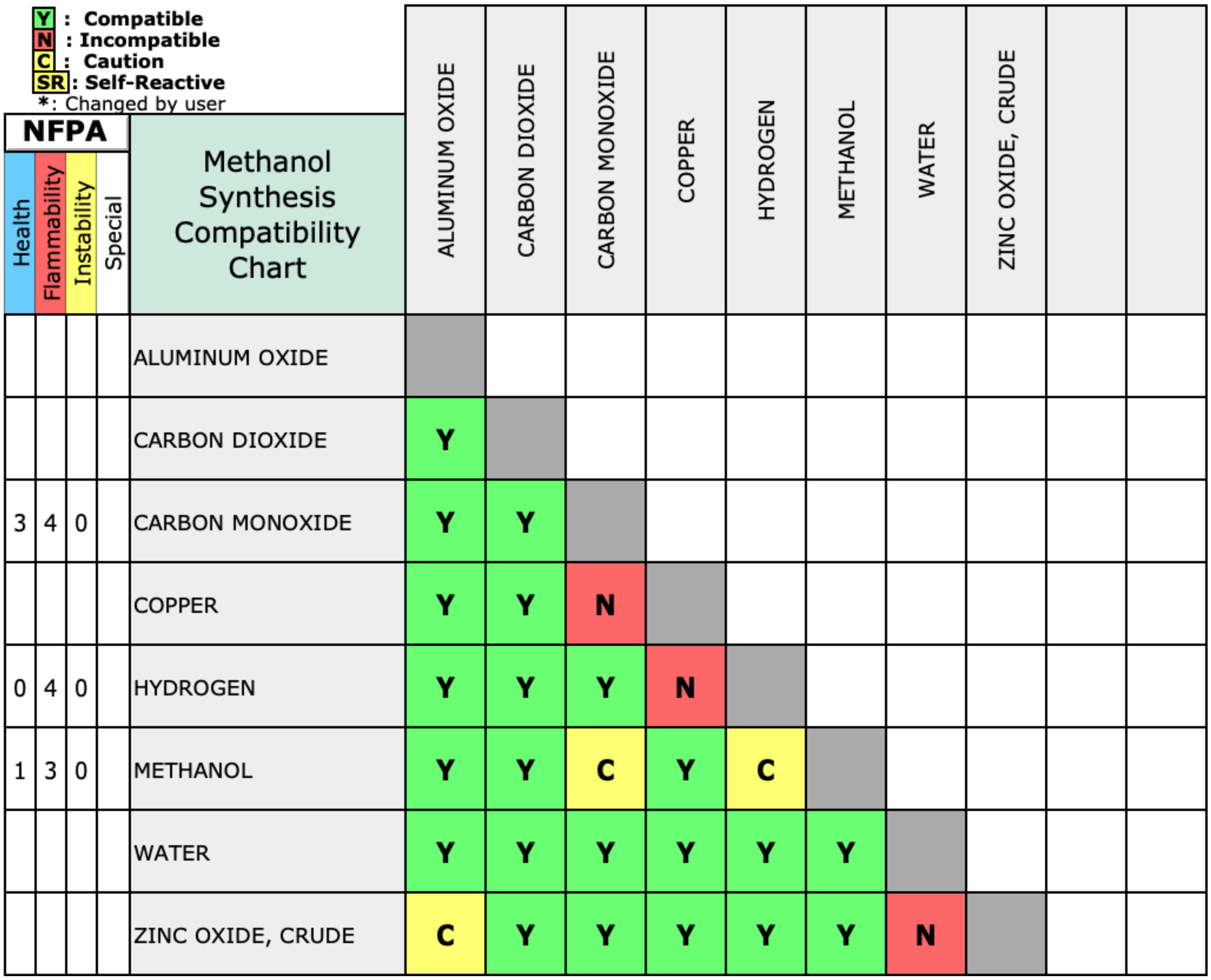
6.1.2. Methanol Synthesis Chemical Hazards and Compatibility

The chemicals used in the methanol synthesis can cause health concerns from prolonged exposure, and so proper precautions must be taken into consideration should any unwanted leaks or accidents occur. In **Table 6.1.2-1,** the chemical compatibility as well as the NFPA values for all chemical components involved in the methanol synthesis process is shown. This table was obtained from the Chemical Reactivity Worksheet, a program developed by National Oceanic and Atmospheric Administration and the Office of Emergency Management of the U.S. Environmental Protection Agency, in collaboration with the Dow Chemical Company and the Center for Chemical Process Safety.

There are multiple compounds that are important to consider. First, exposure to carbon monoxide can cause adverse symptoms within 2 hours of exposure. Carbon monoxide poisoning can cause headaches, weakness, upset stomach, dizziness, vomiting, chest pains and confusion; prolonged exposure can cause death (Center for Disease Control and Prevention, 2021).

Ingestion of methanol can also cause adverse health effects; the most prominent impact of exposure being blindness. Methanol poisoning or prolonged, severe methanol exposure can degrade the optic nerves and also cause nervous system damage, as well as difficulty walking properly, also known as Parkinsonism (Center for Disease Control and Prevention, 2011).

Table 6.1.2-1 Chemical Compatibility Chart for Methanol Synthesis



Y : Compatible
N : Incompatible
C : Caution
SR: Self-Reactive
*: Changed by user

NFPA				Methanol Synthesis Compatibility Chart	ALUMINUM OXIDE	CARBON DIOXIDE	CARBON MONOXIDE	COPPER	HYDROGEN	METHANOL	WATER	ZINC OXIDE, CRUDE		
Health	Flammability	Instability	Special											
				ALUMINUM OXIDE										
				CARBON DIOXIDE	Y									
3	4	0		CARBON MONOXIDE	Y	Y								
				COPPER	Y	Y	N							
0	4	0		HYDROGEN	Y	Y	Y	N						
1	3	0		METHANOL	Y	Y	C	Y	C					
				WATER	Y	Y	Y	Y	Y	Y				
				ZINC OXIDE, CRUDE	C	Y	Y	Y	Y	Y	N			

6.2 Mechanical, Explosion, and Flammable Hazards

As shown in the table, multiple components are highly flammable and proper fire safety precautions must be taken into consideration. Some examples can include installing a proper fire hose system built into the process, or a proper automatic emergency shutdown process. Naturally, all operators should wear proper PPE when on site, including flame resistant clothing (FRC). Pressure vessel explosions must be considered as this process includes multiple pressure vessels. Storage tanks containing both feed hydrogen and the methanol product could potentially pose risks of fires or a boiling liquid expanding vapor explosion (BLEVE). Proper mitigation steps must be put in place in order to ensure that these risks for both fire and explosions are prevented.

Another major concern in our process is the conveyors. These pose a mechanical hazard to the operators and technicians as there are a lot of moving parts. In order to prevent physical injury to any limbs or extremities, operators should avoid putting any body parts near moving parts when in operation and a proper shut down should be performed so that moving parts do not randomly begin operation again during maintenance.

6.3. Safety Culture

In order to maintain a strong safety culture and practices on site, sufficient training should be provided to all employees. Safety procedures and practices must be understood at all levels, and good communication between operators, engineers, and managers must be maintained. This will promote a system of continuous improvement for the plant. In addition to different safety procedures, having the proper enforcement of protocols is key. This enforcement comes with a healthy safety culture. Culture, in this context, should be interpreted as “the shared values and beliefs that interact with an organization's structures and control systems to produce behavioral norms” (Unnerstall, 2020). Having this culture for safety be applied in all levels of a company will give employees of all levels opportunities to voice their concerns and thus prevent accidents that could potentially occur. Furthermore, with a company reinforcing safety as a core value as well as the first and foremost priority, it will drive home the necessity for transparency.

VII. SOCIAL CONSIDERATIONS

7.1 Social Impacts

With direct air capture technology in its infancy, it has the potential to have significant impacts on society and it is important to talk about these impacts and its integration.

Aside from being a method to produce and sell CO_2, direct air capture also serves as a way to combat climate change. In December of 2015, the Paris Agreement was signed by 196 parties across the globe with the long-term goal of limiting the temperature increase of the planet to less than 2°C (*The Paris Agreement)*. To reach this goal, 10 gigatons of carbon dioxide need to be removed from the air annually until 2050 (Ozkan, 2021). Based upon estimations of well-known direct air capture plants Ozkan (2021) was able to estimate that nearly 13,000 direct air capture plants would need to be fully operational by 2024 and this would equate to $1.7 trillion dollars in capital investment. Additionally, a plant with a 1 megaton capacity requires up to 7 tons of water and 0.6 square kilometers of land; this would equate to 91,000 tons of water per year and a total land space of 7,800 square kilometers, larger than the entire state of Delaware Ozkan (2021). This capital investment will likely be funded with government assistance which then entails a large impact on the nation's economic budget and therefore society as a whole. With the large total land space needed, there is also the potential impact on residential areas dependent on each individual facility's siting.

7.2 Facility Siting

The facility will be located in Baytown, Texas, selected for the proximity to a blue hydrogen facility. As a large amount of hydrogen is required for this process, placing it next to a blue hydrogen facility would allow a feedstock to be sent directly to the methanol synthesis processes; this removes the need for large hydrogen storage tanks and allows for an inherently safer design of the facility as a whole.

VIII. FINAL RECOMMENDED DESIGN

8.1. Direct Air Capture

Air Contacting

Block 1 is centered around the Air Contactor unit. The design specifications of this central reactor are limited to conditions as well as flowrate as it was not designed in this report. This block also features two pumps to send the K_2CO_3 rich stream to Block 2, and to transport the KOH rich stream from Block 2 to the Air Contactor. A list of the major equipment pieces needed for Block 1 and their relevant streams are included in **Table 8.1-1** as well as a summary of the equipment, their design specifications, and conditions.

Table 8.1-1 Equipment Summary for Air Contacting

Equipment ID	Equipment Type	Description	Relevant Streams	Design Specifications
R-101	Reactor	Forced-draught Cooling Tower Inspired	1, 2, 3, 4	Unit: N/A (Not designed in this report) Temperature: 21°C Pressure: 1 Bar Flowrate:10783205kmol/hr
P-101	Pump	Centrifugal Pumps	3	Not yet designed
P-102	Pump	Centrifugal Pumps	3	Not yet designed

Pellet Reactor

Block 2 is centered around the Pellet Reactor unit. This block features the main pellet reactor, a conveyor to transport the solids from the pellet reactor, and a heater. A list of the major equipment pieces needed for Block 2 and their relevant streams are included in **Table 8.1-2** as well as a summary of the equipment, their design specifications, and conditions.\

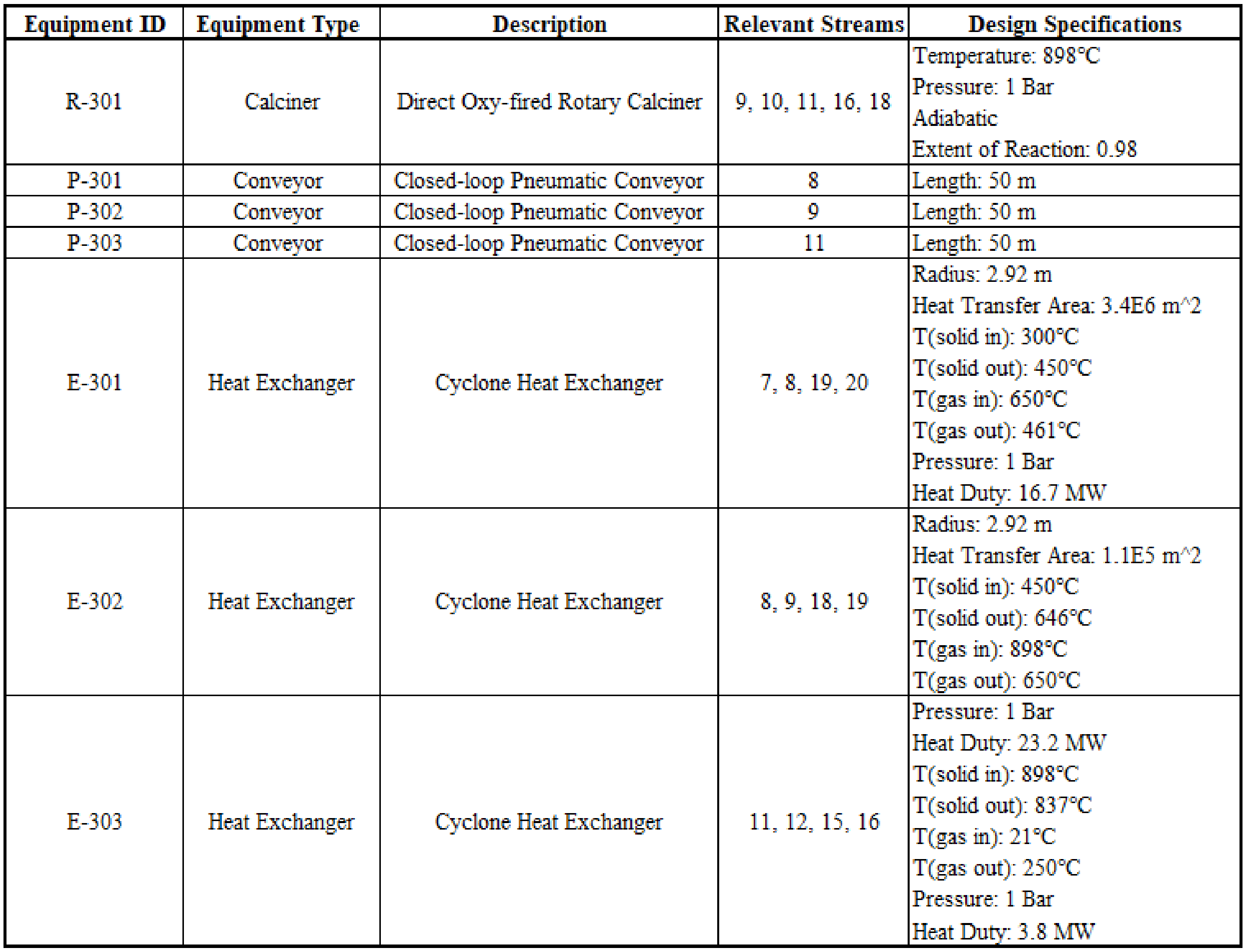
Table 8.1-2 Equipment Summary for Pellet Reactor

Equipment ID	Equipment Type	Description	Relevant Streams	Design Specifications
R - 201	Pellet Reactor	Fluidized Bed Reactor, Crystallizer	5, 6, 14	Temperature: 25°C Pressure: 1 Bar Pellet Size: >0.85mm Fluidization Velocity: 300m/hr Height: 7m Diameter: 4m Volume: 87.7m3 Flowrate: 426883 kmol/hr
P - 201	Conveyor	Solid transport from R-201 to E-201	6	Not yet designed
E - 201	Heater	Heat $CaCO_3$ Pellets	6, 7	T(in): 27°C T(out): 300°C Pressure: 1 Bar Heat Duty: 32.5MW Flowrate: 3742 kmol/hr

Calciner

Block 3 requires 3 solid transfer conveyors, 3 solid-gas heat exchangers and a calciner. Due to a lack of published research on the kinetics surrounding the decomposition reaction occurring in the calciner, the dimensions of the reactor could not be determined; however, the operating conditions are established. A list of the major equipment pieces needed for Block 2 and their relevant streams are included in **Table 8.1-3.**

Table 8.1-3 Equipment Summary for Calciner



Equipment ID	Equipment Type	Description	Relevant Streams	Design Specifications
R-301	Calciner	Direct Oxy-fired Rotary Calciner	9, 10, 11, 16, 18	Temperature: 898°C Pressure: 1 Bar Adiabatic Extent of Reaction: 0.98
P-301	Conveyor	Closed-loop Pneumatic Conveyor	8	Length: 50 m
P-302	Conveyor	Closed-loop Pneumatic Conveyor	9	Length: 50 m
P-303	Conveyor	Closed-loop Pneumatic Conveyor	11	Length: 50 m
E-301	Heat Exchanger	Cyclone Heat Exchanger	7, 8, 19, 20	Radius: 2.92 m Heat Transfer Area: 3.4E6 m^2 T(solid in): 300°C T(solid out): 450°C T(gas in): 650°C T(gas out): 461°C Pressure: 1 Bar Heat Duty: 16.7 MW
E-302	Heat Exchanger	Cyclone Heat Exchanger	8, 9, 18, 19	Radius: 2.92 m Heat Transfer Area: 1.1E5 m^2 T(solid in): 450°C T(solid out): 646°C T(gas in): 898°C T(gas out): 650°C
E-303	Heat Exchanger	Cyclone Heat Exchanger	11, 12, 15, 16	Pressure: 1 Bar Heat Duty: 23.2 MW T(solid in): 898°C T(solid out): 837°C T(gas in): 21°C T(gas out): 250°C Pressure: 1 Bar Heat Duty: 3.8 MW

Slaker

Block 4 surrounds the slaking of calcium oxide to form calcium hydroxide in a slaker reactor. This block requires a slaker, a slurry mixer, 2 solid transfer conveyors, and a pump. Design specifications of the slaker, R-401, are outside the scope of this project due to time constraints; however, the operating conditions are established. A list of the major equipment pieces needed for Block 2 and their relevant streams are included in **Table 8.1-4.**

Table 8.1-4 Equipment Summary for Slaker

Equipment ID	Equipment Type	Description	Relevant Streams	Design Specifications
R-401	Slaker	Refractory Lined Bubbling/Turbulent Fluid Bed	12, 13, 17	Temperature: 300C Pressure: 1 Bar Adiabatic Extent of Reaction: 0.85
R-402	Slurry Mixer	Mixer	13, 3, 14, W4	30% slurry mixture Tank Volume: 141 m^3 Tank Diameter: 6 m Tank Height: 5 m Impeller Type: Pitched Turbine Impeller Diameter: 2 m # of Baffles: 4 Baffle Width: 0.5 m ΔT: 25C
P-401	Conveyor	Closed-loop Pneumatic Conveyor	12	Length: 50 m
P-402	Conveyor	Closed-loop Pneumatic Conveyor	13	Length: 50 m
P-403	Pump	Centrifugal Pump	14	Electrical Draw: 179.5 kW

Water Knockout System

The purpose of Block 5 is to purify the product stream from the calciner to 99.8% of carbon dioxide. The block consists of three compressors, three coolers, and three flash drums to achieve this. The operating specifications listed below in **Table 8.1-5.**

Table 8.1-5 Equipment Summary of Water Knockout System

Equipment ID	Equipment Type	Description	Relevant Streams	Design Specifications
C-501	Compressor	Centrifugal Compressor	20, 21	Outlet Pressure: 3.5 bar Net Work: 27.5 MW
E-501	Cooler	Cooler	21, 22	Temperature Outlet: 100°C Duty: 54.6 MW
F-301	Flash Drum	Flash Drum	22, 23	Drum Volume: 15.4 m^3 Outlet Purity: 0.64
C-502	Compressor	Centrifugal Compressor	23, 24	Outlet Pressure: 12.5 bar Net Work: 13.4 MW
E-502	Cooler	Cooler	24, 25	Temperature Outlet: 45°C Duty: 36.5 MW
F-502	Flash Drum	Flash Drum	25, 26	Drum Volume: 2.7 m^3 Outlet Purity: 0.993
C-503	Compressor	Centrifugal Compressor	26, 27	Outlet Pressure: 42.9 bar Net Work: 8.2 MW
E-503	Cooler	Cooler	27, 28	Temperature Outlet: 40°C Duty: 9.3 MW
F-503	Flash Drum	Flash Drum	28, 29	Drum Volume: 0.6 m^3 Outlet Purity: 0.998

8.2. Methanol Synthesis

Reverse Water Gas Shift Reactor

Block 7 involves the production of carbon monoxide through the reverse water gas shift reaction. This block is made up of five pumps, one reactor, three heat exchangers, and a flash drum. A list of the needed equipment are provided in the table below, alongside the relevant streams and design specifications.

Table 8.2-1 Equipment Summary for Reverse Water Gas Shift Reactor

Equipment ID	Equipment Type	Description	Relevant Streams	Design Specifications
R-701	Reactor	Heterogeneous Packed Bed Reactor	32, 33	Temperature: 500°C Pressure: 10.1 Bar Catalyst Diameter: 0.25 m Height: 2 m Diameter: 0.05 m Volume: 198 m3 Flowrate: 67540.2 kmol/hr Tubes: 12568 Pressure Drop: 0.05 bar
PV-701	Valve	N/A	33	N/A
E-701	Heat Exchanger	Heat Reactant Gas Sream	32	Heat Transfer Area: 1759 m2 Number of Exchangers: 1 Number of tubes: 6052 Tube Length: 5 m Tube OD: 0.02 m T(Gas in): 33°C T(Gas Out): 500°C T(Steam in): 600°C T(Steam out): 334°C Steam Flow: 80000 kmol/hr
E-702	Heat Exchanger	Cool Reactor Effluent Stream and Produce Steam	33	Heat Transfer Area: 1087 m2 Number of Exchangers: 1 Number of tubes: 3736 Tube Length: 5 m Tube OD: 0.02 m T(Gas in): 500°C T(Gas Out): 180°C T(Water in): 30°C T(Steam out): 153°C Water Flow: 15000 kmol/hr
E-703	Heat Exchanger	Cool Reactor Effluent Stream for Flash Drum	33	Heat Transfer Area: 8027 m2 Number of Exchangers: 8 Number of tubes: 27612 Tube Length: 5 m Tube OD: 0.02 m T(Gas in): 180°C T(Gas Out): 35°C T(Water in): 30°C T(Water out): 64°C Water Flow: 200000 kmol/hr
F-701	Flash Drum	Seperates Vapor and Liquid Streams from Reactor Effluent	33, 34, 35	Diamter: 6 m Height: 24 m

Methanol Synthesis Reactor

Block 8 encompasses the production of methanol. Utilizing the carbon monoxide stream from the previous reactor this reactor produces methanol. This block consists of seven pumps, one reactor, three heat exchangers, and a flash drum. A list of the major equipment pieces are and their design specifications are summarized in **Table 8.2-2**.

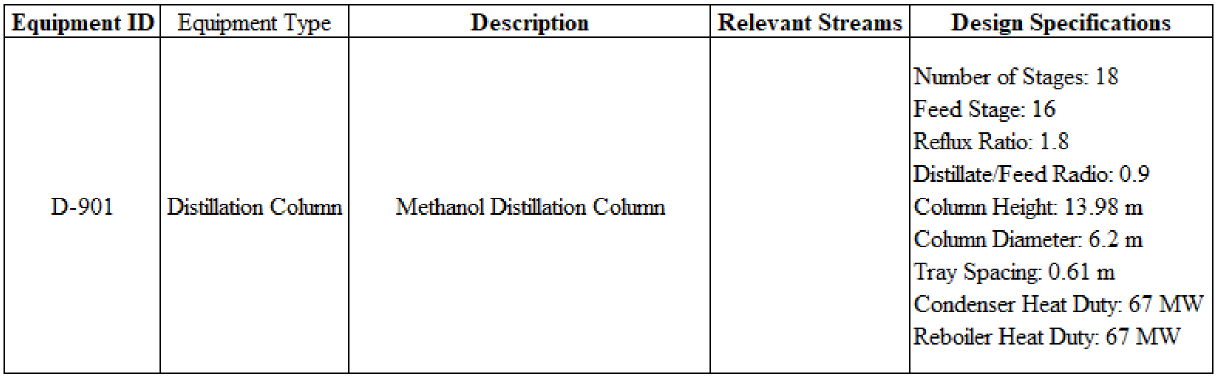
Table 8.2-2 Equipment Summary for Methanol Synthesis Reactor

Equipment ID	Equipment Type	Description	Relevant Streams	Design Specifications
R-801	Reactor	Heterogeneous Packed Bed Reactor	37, 38	Temperature: 250°C Pressure: 30.4 Bar Catalyst Diameter: 0.016 m Height: 7 m Diameter: 0.1 m Volume: 149 m3 Flowrate: 20884.1 kmol/hr Tubes: 676 Pressure Drop: 0.3 bar
C-801	Pump	Centrifugal	37	Duty: 33 MW
C-802	Pump	Centrifugal	38	Duty: 12 MW
E-801	Heat Exchanger	Heat Reactant Gas Sream	37	Heat Transfer Area: 29 m2 Number of Exchangers: 1 Number of tubes: 100 Tube Length: 5 m Tube OD: 0.02 m T(Gas in): 35°C T(Gas Out): 250°C T(Steam in): 600°C T(Steam out): 348°C Steam Flow: 2000 kmol/hr
E-802	Heat Exchanger	Cool Reactor Effluent Stream and Produce Steam	38	Heat Transfer Area: 261 m2 Number of Exchangers: 1 Number of tubes: 898 Tube Length: 5 m Tube OD: 0.02 m T(Gas in): 250°C T(Gas Out): 180°C T(Water in): 30°C T(Steam out): 160°C Water Flow: 2000 kmol/hr
E-803	Heat Exchanger	Cool Reactor Effluent Stream for Flash Drum	38	Heat Transfer Area: 2910 m2 Number of Exchangers: 3 Number of tubes: 10010 Tube Length: 5 m Tube OD: 0.02 m T(Gas in): 180°C T(Gas Out): 35°C T(Water in): 30°C T(Water out): 71°C Water Flow: 50000 kmol/hr
F-801	Flash Drum	Seperates Vapor and Liquid Streams from Reactor Effluent	38, 39, 40	Diameter: 2 m Height: 6 m

Distillation Column

Block 9 consists of a distillation column to purify methanol in the liquid distillate stream. The specifications for this distillation column are as follows in the table below.

Table 8.2-3 Equipment Summary for Distillation Column



Equipment ID	Equipment Type	**Description**	**Relevant Streams**	**Design Specifications**
D-901	Distillation Column	Methanol Distillation Column		Number of Stages: 18 Feed Stage: 16 Reflux Ratio: 1.8 Distillate/Feed Radio: 0.9 Column Height: 13.98 m Column Diameter: 6.2 m Tray Spacing: 0.61 m Condenser Heat Duty: 67 MW Reboiler Heat Duty: 67 MW

IX. CONCLUSION AND RECOMMENDATIONS

Direct carbon air capture is an exciting new technology that allows for hope that the world can reverse the scale of post-industrial greenhouse gas emissions and halt the damaging effects of rapid climate change. Being able to use the carbon dioxide in a downstream process to produce a desirable product only adds to this positive outlook, inspiring the design of the proposed Direct Air Capture and Methanol Synthesis process. Though, given current technology and pricing, improvements must be made to allow for this project to be a worthy investment.

With an IRR of 1.47%, this project is close to being viable, but there is still a necessity to improve the economic outlook. Therefore, it cannot be recommended that the plant be constructed due to the high capital and operational costs associated in conjunction with the base-scenario revenue.

When considering alternative scenarios, there is optimism in regard to economic viability. From section 4.6, it can be seen that when methanol is sold at a premium price, the plant can become profitable after its first year online. If the market allowed for this, the DAC to methanol synthesis project could be a worthy investment. This report recommends serious consideration into premium pricing as well as the selling of carbon credits.

In regard to the DAC system, as mentioned, this is still an emerging technology. Innovations in carbon capture are still being explored with the hope of increasing cost efficiency to remove ambient carbon dioxide. Specifically for this project, there is room for general optimization within the plant that did not fall under the scope of this report. Given the opportunity, this report would have re-configured and optimized the heat exchanger design, given its large portion of equipment purchasing and operating costs. Additionally, the water knockout system is costly in terms of capital and required utilities. This system could be removed and the downstream methanol synthesis process could be redesigned to handle extra water in the carbon dioxide stream. Moreover, if the water knockout system remains in place, additional coolers could be added to decrease compressor duty. Finally, renewable energy could be integrated into this design to provide necessary power and thus reduce utility costs.

In regard to the methanol synthesis system, as mentioned in section 3.3.5, redesigns should be conducted based off of an improved material balance. Additionally, a few recommendations for future work can be made. The first begins with C-802; this compressor was designed to pressurize the stream to optimize for the separation of methanol, but this further pressurization will cause an increase in operating costs. An economic analysis for this compressor could be performed to determine if this extra pressurization results in a loss or profit for the plant. Another way to potentially save money for the plant would be to recycle the vapor distillate from the distillation column back to the reactors as this stream is still rich in carbon dioxide. Currently, this stream is being flared as a means to remove any impurities, primarily nitrogen, deriving from the DAC portion of the process. If the recycling of this stream were to be added, a flare elsewhere in the process would need to be added. Lastly, there is room for optimization on the distillation column of the final product separation. An analysis on the location of the feed stage could be done to possibly provide a more optimal separation.

Aside from DAC technological advancements and plant optimization, this report also hopes that hydrogen production technology will advance so that the necessary feed of hydrogen is less expensive. Currently, this report uses blue hydrogen for methanol synthesis, though, the intention of this project is to use hydrogen formed from sustainably powered electrolysis. However, this type of green hydrogen is too expensive to evaluate.

X. ACKNOWLEDGMENT

With gratitude, we acknowledge Professor Eric W. Anderson of the University of Virginia chemical engineering department for his support and advising throughout the synthesis of this report. We would also like to acknowledge Professor Gaurav Giri for his counsel on the pellet reactor design as well as Professor George Prpich for his emotional support and relevant conversation. Additionally, we would like to acknowledge the capstone team of Anna Winter, Ben Newhouse, Samuel Ong, Peter Sepulveda, and Karl Westendorff and their 2021 report "Design of a Thorium Extraction Process from Monazite Sand", which offered guidance for organization and content. Finally, we would like to acknowledge Taco Bell for getting the authors of this report through hard times.

XI. TABLE OF NOMENCLATURE

Symbol	Unit	Description
-	Mt-CO2/year	megatonne of carbon dioxide per year
-	t-CO2/year	tonne of carbon dioxide per year
G	m/s	growth rate of $CaCO_3$ pellets
K_g	-	linear growth rate coefficient
SV	m/h	superficial velocity
L_0	mm	seed pellet size
S	kg solute/kg water	supersaturation
L_m	m	mean crystal size
τ	s	residence time
v	m/s	volumetric flowrate
N_{JS}	1/s	"just-suspended" impeller speed
s		Zwietering geometrical constand
ϑ	kg/m·s	dynamic viscosity
ρ_L	kg/m^3	liquid density
ρ_v	kg/m^3	vapor density
X	%	solid to liquid mass percentage
d_p	m	particle diameter
g	m/s^2	acceleration due to gravity
Re		Reynolds Number
N	1/s	impeller speed
μ	m^2/s	kinematic viscosity
ρ_{slurry}	kg/m^3	slurry density
c_w	%	solid concentration percentage by weight
ρs	kg/m^3	solid density
Np		Power Number
P	J/s	power
$m_{cooling\ water}$	kg/s	mass flowrate of cooling water
Q	W	heat duty
C	J·kg·K	specific heat
u	m/s	maximum allowable vapor velocity
k	m/s	standard value of 0.107 to account for unit
ΔTm	K	log-mean temperature
T_g	C	temperature of gas stream

Q_t	J	Heat transfer rate
m_s	Kg	solid mas
At	M^2	heat transfer area
h	W/m^2·K)	heat transfer coefficient
c_{ps}	J/kj·K	specific heat of solid
Nu	-	Nusselt Number
F_m	-	Solid loading ratio
D_c	m	diameter of cyclone heat exchanger
Pr	-	Prandtl number
h_p	W/m^2·K	gas- particle heat transfer coefficient
μ_g	Pa·s	dynamic viscosity of gas
ρ_g	kg/m^3	density of gas
Δp	Pa	pressure drop
μ	N/m^2	fluid viscosity
ϵ	m^3	void space
u_{of}	m/s	fluid superficial velocity
GHSV	mL/g·hr	gas hourly space velocity
V_o	mL/hr	exhaust flow rate
M_c	g	mass of catalyst
U	W/m^2·K	overall heat transfer coefficient
ΔT	K	temperature difference
h_o	W/m^2·K	heat transfer coefficient on outer fluid
h_i	W/m^2·K	heat transfer coefficient on inner fluid
r_i	m	inner radius of reactor tube
r_o	m	outer radius of reactor tube
k	W/m·K	thermal conductivity
ΔH	J/mol	heat of vaporization
N_{min}	-	minimum number of stages
X_d	mol x/mol	distillate composition
X_b	mol x/mol	bottom composition
X_{LK}	mol x/mol	light key composition
X_{HK}	mol x/mol	heavy key composition
$\alpha_{LK,HK}$	-	relative volatility

XII. REFERENCES

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XIII. APPENDIX A - Sample Calculations

Sample Calculation A.1 - Pellet Reactor Sizing:

Assumptions:

$SV = 300\, m/hr$

$L_0 = 0.0001\, m$

$S = 84.4\, kg\ solute/kg\ water$

$L_m = 0.00085\, m$

$R_{HD} = H/D = 2$

$$G = 1.0064 * 10^{-18} * SV^{2.818} * L_0^{-0.6556} * S^{1.9353} \quad \text{[m/s]}$$

$$G = 1.0064 * 10^{-18} * (300)^{2.818} * (0.0001)^{-0.6556} * (84.4)^{1.9353}$$

$$G = 2.33 * 10^{-7}\, m/s$$

$$L_m = \frac{G*\tau}{4}$$

$$\tau = \frac{4*L_m}{G}$$

$$\tau = \frac{4*(0.00085)}{2.33*10^{-7}} = 1780\, s = 28.6\, min = 0.49\, hr$$

$$V = \tau * \nu = (1780\, s) * (0.0384\, m^3/s) = 66\, m^3$$

$$D = \sqrt[3]{\frac{4V}{\pi}} = \sqrt[3]{\frac{4*66\, m^3}{\pi}} = 3.48\, m$$

$$H = 2 * 3.48 = 6.95\, m$$

Sample Calculation A.2 - Slurry Mixer Sizing and Power Consumption:

Assumptions:
τ = 15 min
v = 0.119 m^3/s
H/D = 0.8
s = 6.5
v= 9.78E-7 m^2/s
G = 9.81 m^2/s
$\Delta\rho$ = 1210 kg/m^3
ρ_L= 1000 kg/m^3
X = 94.8
DI = 2 m
d_p= 0.00085 m
$c_w = 30$
$N_P = 6$

$$V = (0.119\, m^3/s)(15 min * 60 \frac{s}{min}) = 107.5\, m^3$$

$$D = (\frac{107.5\, m^3}{\pi*0.25*0.8})^{(1/3)} = 5.6\, m \rightarrow 6\, m$$

$$H = 0.8 * 5.6\, m = 4.4\, m \rightarrow 5\, m$$

$$\rho_{slurry} = \frac{100}{\frac{c_w}{\rho_s} + \frac{100 - c_w}{\rho_L}}$$

$$\rho_{slurry} = \frac{100}{\frac{30}{2120} + \frac{100-30}{1000}} = 1188 \text{ kg/m}^3$$

$$N_{JS} = sv^{0.1}(\frac{g\Delta\rho}{\rho_L})^{0.45} X^{0.13} d_p^{0.2} DI^{-0.85}$$

$$N_{JS} = (6.5)(9.78 * 10^{-7})^{0.1} (\frac{g*1210\, kg/m^3}{1000\, kg/m^3})^{0.45} (94.8)^{0.13} (0.00085\, m)^{0.2} (2\, m)^{-0.85}$$

$$N_{JS} = 1.21 \text{ 1/s}$$

$$P = N_p \rho_{slurry} N^3 DI^5$$

$$P = (6)(1188\ kg/m^3)\ (1.21\ 1/s)^3(2\ m)^5$$

$$P = 403\ \text{kW}$$

Sample Calculation A.3 - E-201 Heat Duty:

Assumptions:

$c_p = 0.8343\ J/g\ C$

ΔT = 300 -27 = 273 C

m = 374476 kg/hr (calcium carbonate pellets)

$$Q = m\ {*}c_p{*}\Delta T = (374476\ \text{kg/hr}){*}(0.8343\ \text{J/g*C}){*}(273\ \text{C})$$

$$Q = 23.7\ {*}\ 10^7\ J/s = 23.7\ \text{MW}$$

Sample Calculation A.4 - Cyclone Heat Exchanger Heat Transfer Area and Sizing

Assumptions:

$c_{ps} = 1508.1\ j/kg\ C$

$h = 250\ W/Km^2$

$$\Delta T = \frac{(T_{Gin} - T_{Sin}) - (T_{Gout} - T_{Sout})}{\ln\left(\frac{T_{Gin} - T_{Sin}}{T_{Gout} - T_{Sout}}\right)}$$

$$\Delta T = \frac{(650 - 300) - (461 - 450)}{\ln\left(\frac{650 - 300}{461 - 450}\right)} \quad = 94.09C$$

$$Q = m_s c_{ps}(T_{Sout} - T_{Sin})$$

$$Q = 138.2\frac{kg}{s} \cdot 1508.1\frac{J}{kg \cdot C}(450 - 300)K \quad = 4.29 \cdot 10^{10}\frac{J}{s}$$

$$A = \frac{Q}{h \cdot \Delta T}$$

$$A = \frac{4.29 \cdot 10^{10}\frac{J}{s}}{250\frac{W}{m^2K} \cdot 370.97K} = 9.13 \cdot 10^5\ m^2$$

$$Nu = 1300 \cdot Re^{0.41}F_m^{0.47}\left(\frac{2 \cdot d_p}{D_c}\right)Pr^{\frac{1}{3}}$$

$$Nu = \frac{h_p D_c}{k_a}$$

$$Re = \frac{\vartheta_c D_c \rho_g}{\mu_g}$$

$$Pr = \frac{c_{pa} D_c \mu_g}{k_g}$$

$$Pr = \frac{1508.1 \frac{J}{kgK} \cdot 0.0000324 \frac{N}{m^2}}{0.0671 \frac{w}{mk}} = 0.735$$

$$F_m = \frac{m_s}{m_a}$$

$$F_m = \frac{3741613^{0.47}}{64.85}$$

$$D_c \ = \sqrt[2.41]{\frac{1300 \cdot \left(\frac{4\dot{V}\rho_g}{\pi \mu_g} \right)^{0.41} F_m^{0.47} \cdot 2 \cdot k_g D_p Pr^{1/3}}{h_p}}$$

$$D_c \ = \sqrt[2.41]{\frac{1300 \cdot \left(\frac{4 \cdot 113.2m^3 \cdot 0.576 \frac{kg}{m^3}}{\pi \cdot 0.0000324 \frac{N}{m^2}} \right)^{0.41} \ 5.78 \cdot \ {10^3}^{0.47} \cdot 2 \cdot 0.0671 \frac{w}{mk} \cdot 0.00085\, m \ \cdot 0.735^{1/3}}{250 \frac{W}{m^3 K}} = 2.9m}$$

Sample Calculation A.5 - Cooling Water for Heat Exchange

All hand calculated cooling water amounts were found via the same format, as such, only one sample calculation will be provided for this report.

Assumptions:

c_{ps} = Weighted average of heat capacities of compound’s present at appropriate temperature

$$m_{Cooling\ Water} = \frac{Q}{C\Delta T}$$

$$m_{Cooling\ Water} = \frac{54635\ W}{1209.6\ J/KgC * (707.209-100)C} = 74.4\frac{kg}{s} * \frac{3600\frac{s}{hr}}{18\frac{kg}{kmol}} = 14877.3\ \frac{kmol}{hr}$$

Sample Calculation A.6 -Flash Drum Calculations

All hand calculated flash drum parameters follow the same format, as such, only one sample calculation will be provided for this report.

Assumptions:

K = 0.107 m/s

$L = 2.5D$

Per the Souders-Brown equations.

$$u = (k)\sqrt{\frac{\rho_L - \rho_v}{\rho_v}} = 0.107*\sqrt{\frac{918\frac{kg}{m^3} - 4.24\frac{kg}{m^3}}{4.24\frac{kg}{m^3}}} = 1.57\ \frac{m}{s}$$

$$A = \frac{V}{u} = \frac{15.43\frac{m^3}{s}}{1.57\frac{m}{s}} = 9.82\ m^2$$

$$D = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4*9.82\ m^2}{\pi}} = 3.54\ \text{m}$$

L = 2.5*D = 3.54m*2.5 = 8.83m

Sample Calculation A.7 - Distillation Column Calculations

To calculate the minimum number of stages for the distillation column, the fenske equation was used as a preliminary value before optimization through Aspen.

Per the Fenske Equation.

$$N_{min} = log[(\frac{X_d}{1-X_d})(\frac{1-X_b}{X_b})] \ / \ log[\alpha_{avg}]$$

$$3.6 = log[(\frac{0.1}{1-0.1})(\frac{1-0.9}{0.9})] \ / \ log[3.38]$$

Sample Calculation A.8 - Heat Exchanger Condenser/Reboiler

Surface area required for the reboiler and condenser for the distillation column unit.

Per General Heat Transfer Equation.

$$Q = UA\Delta T$$

$$A = (\frac{10000}{0.85 * 15})$$

$$A = 784.3$$

Sample Calculation A.9 - Ergun

Calculates pressure drop in reactor units.

Assumptions:
L = 7 m
d_p = 0.016 m

Per Ergun Equation.

$$\frac{\Delta p}{L} = \frac{150u_f (1-\epsilon)^2 u_o}{\epsilon^3 d_p^2} + \frac{1.75(1-\epsilon)\ \rho_s\ u_{fo}^2}{\epsilon^3 d_p}$$

$$\frac{\Delta p}{7} = \frac{150 * 0.00002 * (1-0.75)^2 * 7.57}{0.75^3 * 0.016^2} + \frac{1.75 * (1-0.75) * 1.15 * 7.57^2}{0.75^3 * 0.016}$$

$$\Delta p = 0.295\ atm$$

Sample Calculation A.10 - Reactor Volume

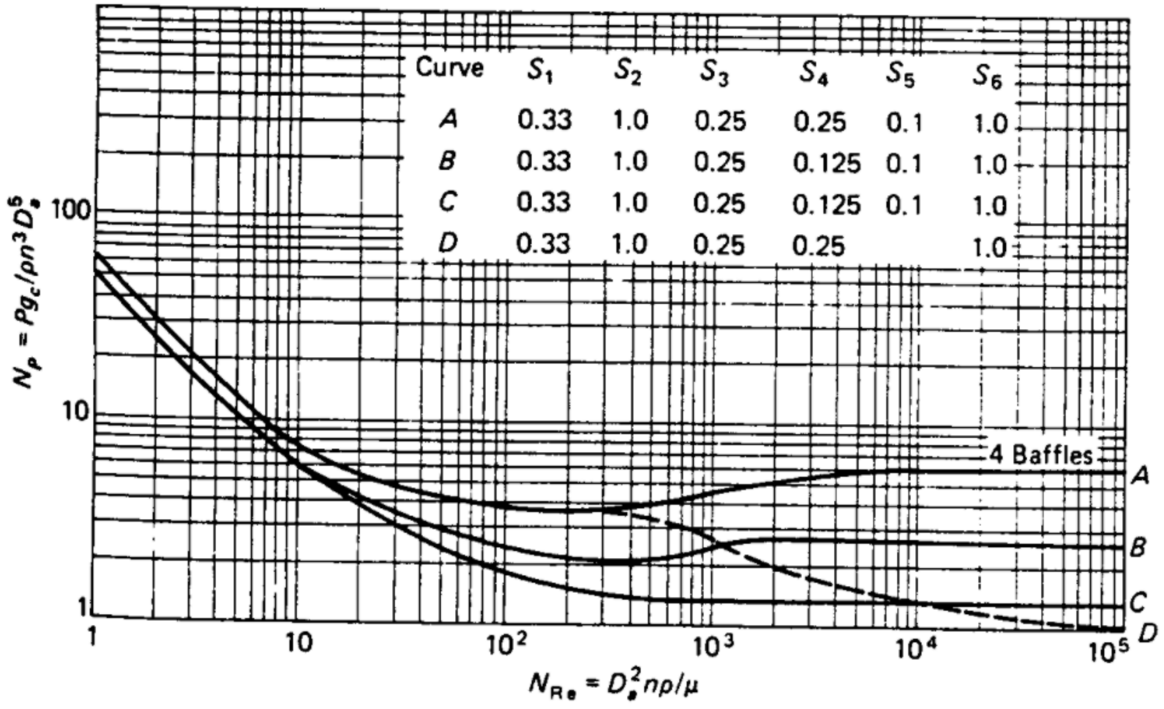
Calculates pressure drop in reactor units.

Per Residence Time equation.

$$\tau = V/v$$
$$V = \tau/v$$
$$V = \frac{0.064\ s}{3084.4\ m^3/s} = 197.4\ m^3$$

XIV. APPENDIX B - Correlation Plots

Figure A.B-1: Reynold’s Number and Power Correlation Plot



Curve	S_1	S_2	S_3	S_4	S_5	S_6
A	0.33	1.0	0.25	0.25	0.1	1.0
B	0.33	1.0	0.25	0.125	0.1	1.0
C	0.33	1.0	0.25	0.125	0.1	1.0
D	0.33	1.0	0.25	0.25		1.0

Figure A.B-: Purchased Costs for Fired Heaters, Calciner Economic Correlation (See Pyrolysis Furnace

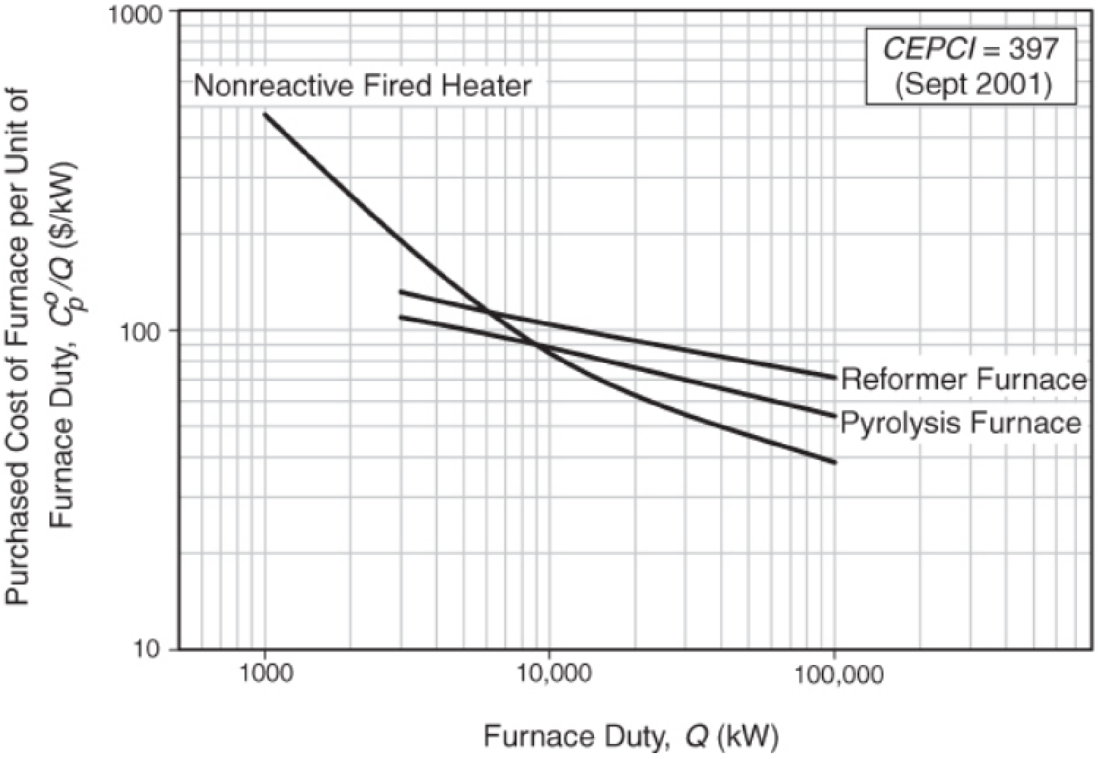
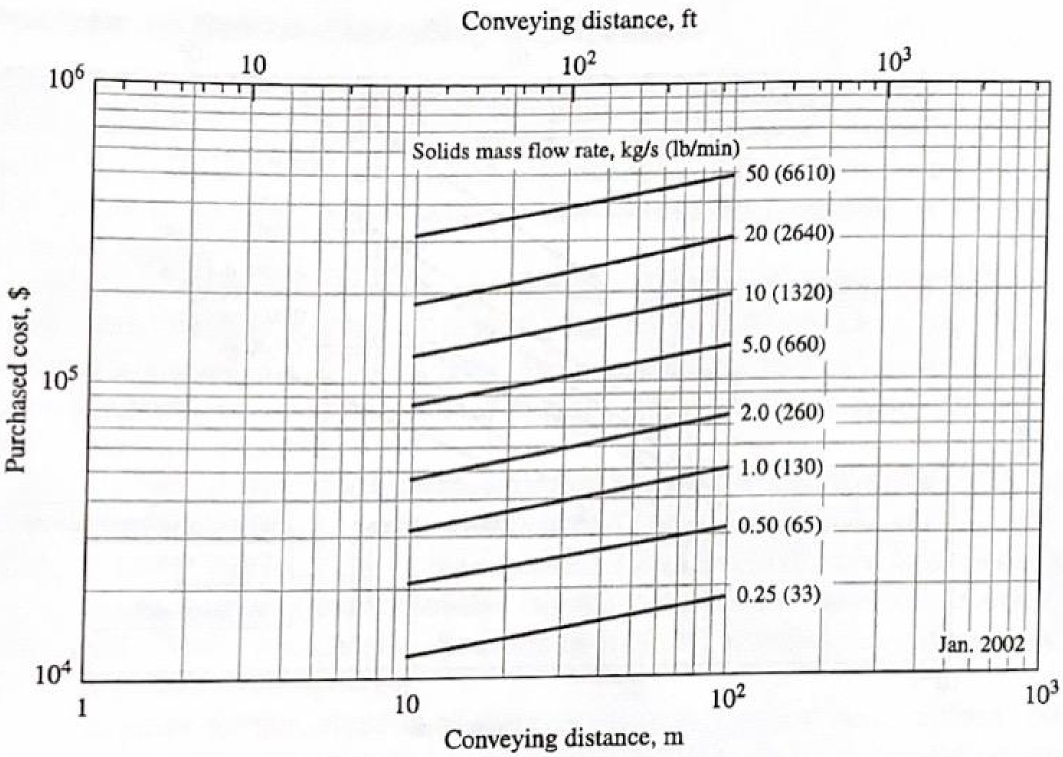
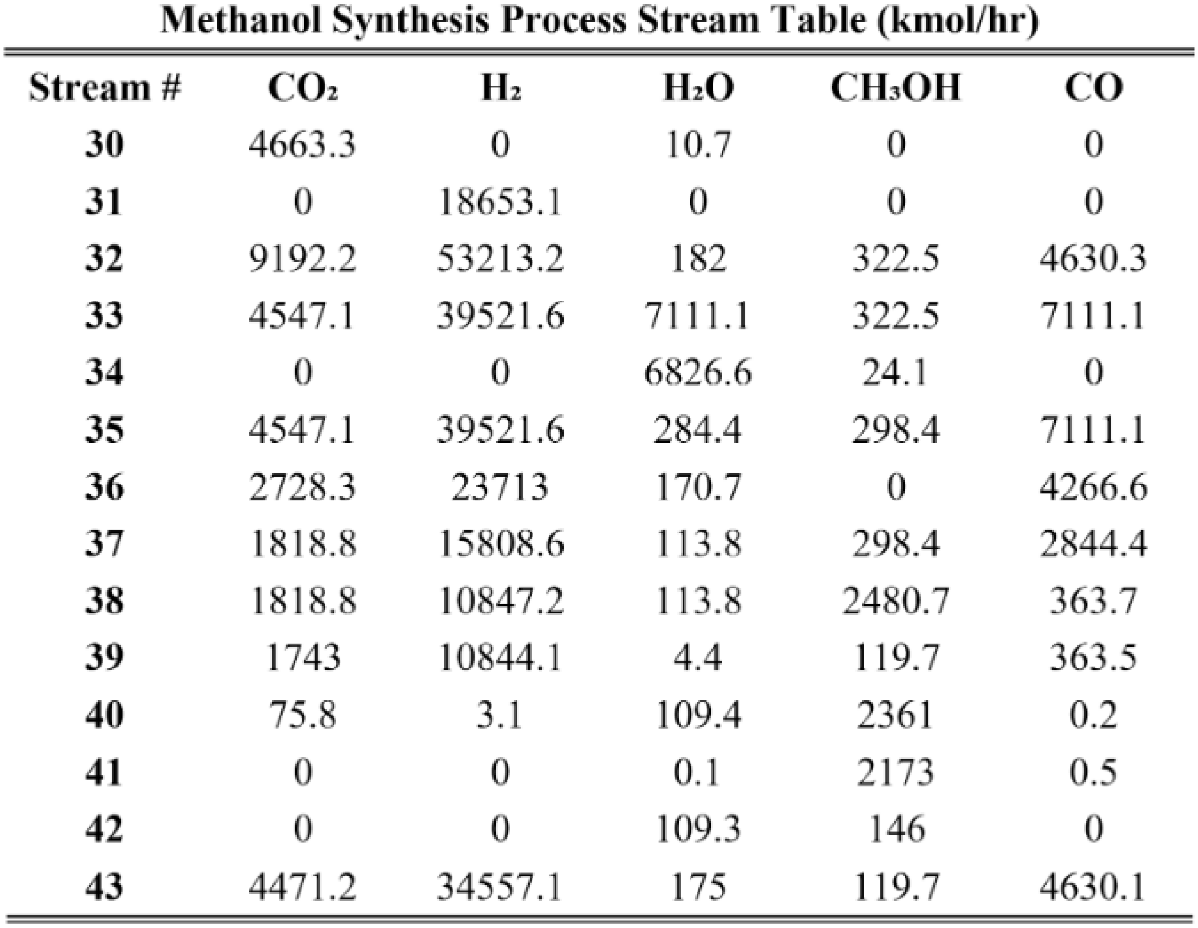


Figure A.B-3: Purchased Cost of Pneumatic Solids-Conveying Equipment (Drivers Included)



XV. APPENDIX C - Preliminary Stream Tables

Figure A.C-1: Preliminary Methanol Synthesis Stream Table



Methanol Synthesis Process Stream Table (kmol/hr)

Stream #	CO_2	H_2	H_2O	CH_3OH	CO
30	4663.3	0	10.7	0	0
31	0	18653.1	0	0	0
32	9192.2	53213.2	182	322.5	4630.3
33	4547.1	39521.6	7111.1	322.5	7111.1
34	0	0	6826.6	24.1	0
35	4547.1	39521.6	284.4	298.4	7111.1
36	2728.3	23713	170.7	0	4266.6
37	1818.8	15808.6	113.8	298.4	2844.4
38	1818.8	10847.2	113.8	2480.7	363.7
39	1743	10844.1	4.4	119.7	363.5
40	75.8	3.1	109.4	2361	0.2
41	0	0	0.1	2173	0.5
42	0	0	109.3	146	0
43	4471.2	34557.1	175	119.7	4630.1