Hydrogen Fueling Station

Project Proposal

Design Team # 1

May 9, 2011

The following report is a detailed engineering proposal for the construction of a hydrogen (H_2) production plant on 2040 8th Ave. in New York City, NY. The purpose of the plant is to convert natural gas into 99.9999% pure H_2 product that will be used as transportation fuel for vehicles.

The main business motivation for this H_2 production plant is the growing global market demand for H_2 due to interest in using H_2 as an alternative transportation fuel. The combination of continuously increasing fuel demand in the US, declining domestic fossil fuel resource availability and production, and rising fossil fuel costs are causing the federal and industrial sectors to invest in alternative fuel sources like H_2. Since natural gas is an abundant resource in the US that is significantly cheaper than conventional fossil fuels, H_2 production from natural gas via steam reformation is an attractive fuel production investment.

The feedstock of the plant is natural gas provided by the Transco pipeline from New Jersey and the products of the plant that will be sold for revenue are 99.9999% pure H_2 and dry ice. For an operating year of 8000 hours, the plant produces 146,100 kilograms of H_2 per year (kg/yr), which is enough to fuel 100 vehicles with a tank size of 4 kg at 700 atmospheres (atm). The plant is designed for a H_2 storage capacity of 24 hours. In addition to H_2, the plant also produces 1.5 million kg of dry ice/yr, 48,000 kg of carbon dioxide (CO_2)/yr, and 283,190 gallons of wastewater/yr. The lifetime of the H_2 plant is 20 years.

The H_2 production technology that is employed in this plant is steam reformation. Steam reformation is the most established commercial method for H_2 production and it is also the cheapest. In this technique, the natural gas feedstock is reacted with high temperature steam to yield H_2. The H_2 product is purified to its 6 nines spec via pressure swing adsorption and the CO_2 by-product is separated from the process stream and converted to dry ice, which is sold for additional revenue to the plant. There are a total of six major stages in the H_2 production process for this plant and they are: pre-treatment, steam reformation, temperature shift reactions, pressure swing adsorption, CO2 absorption, and dry ice production.

The working capital for this H_2 production plant is $113,600 and the overall capital cost is $2,611,444. The total fixed operating cost is $742,405 and the total variable operating cost is $349,155. The H_2 product will be sold at a retail price of $5/kg, and the dry ice will be sold at $0.05/kg. With a 3% inflation

rate, a 35% overall tax rate, and straight-line depreciation, the cumulative cash flow for the plant is a loss of $28 million by the end of the lifetime of the plant. Adjustments in the costs and product rates for the H_2 plant yield a net profit for the plant by the eleventh year of the plant's lifetime. At a H_2 product retail rate of $10/kg, a discount rate of 9.82%, and no inflation, the H_2 plant reaches its breakeven point at 11 years and yields a net profit of approximately $4.5 million by the end of the plant lifetime.

Environmental health and safety considerations were incorporated into the design of the H_2 production plant. The plant has zero emissions of hydrogen sulfide (H_2S) and carbon monoxide (CO), which are toxic intermediate products of the production process. CO_2, which is a greenhouse gas (GHG), is a by-product of this production process. Most of the CO_2 in the plant's process stream is recovered and converted to dry ice and the rest is emitted from the plant at an annual rate of 48,000 kg/yr. Safety precautions were implemented to avoid risk of explosion or gas leakages. These precautions include putting major process equipment underground, using double containment for high pressure vessels, adding temperature and CO detectors to process equipment, and providing intensive safety, process operations, and materials handling training to production plant employees.

LIST OF FIGURES

PROCESS DESIGN SUMMARY

The plant was designed to meet all of the requirements specified in the problem description with minimal energy consumption. In order to balance reliability and efficiency, the design was based on a traditional steam reforming process, but was scaled down and modified to include carbon capture and utility-saving features. A block flow diagram outlining the main components of the plant and the process streams is shown in Figure 1. The following paragraphs briefly summarize the purpose of each section.
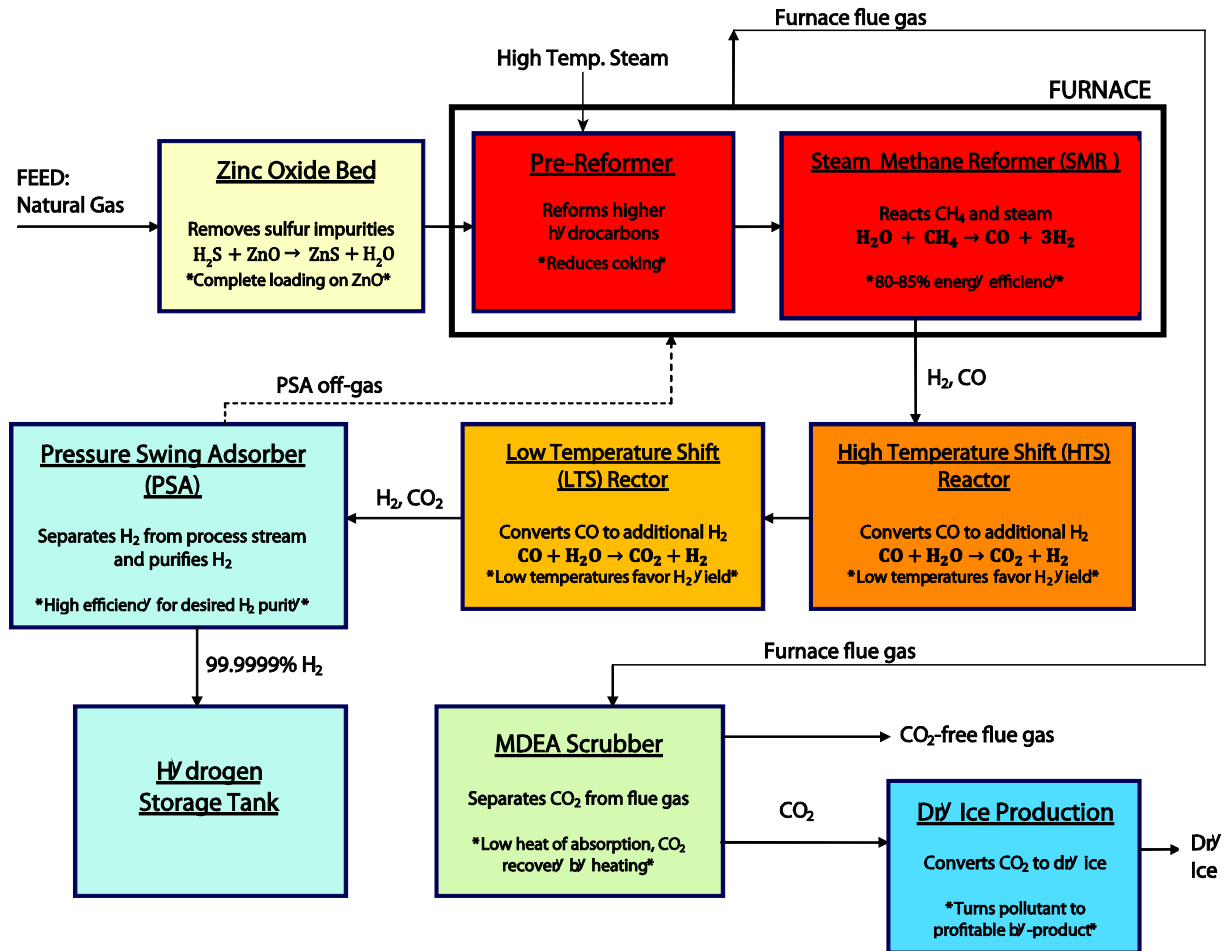
Figure 1: Block Flow Diagram

Zinc Oxide Bed

The zinc oxide (ZnO) bed is an adsorber that is located in the pre-treatment stage of the overall process. The function of the ZnO bed is to remove the H_2S and additional sulfide impurities in the natural gas feedstock before it enters the steam reformation stage. Sulfur removal is essential because sulfur

poisons the catalysts in the reactors of this process consequently impairing catalyst performance and reducing overall production rate. Furthermore, H_2S is a poisonous toxic gas therefore it cannot be emitted from the H_2 plant. The feed to the ZnO bed is the natural gas feedstock and the output is a desulfurized natural gas process stream. ZnO is the adsorbent of choice for desulfurization because it achieves close to complete loading of H_2S.

Furnace

The furnace provides the heat for the reformers, preheats the natural gas and steam, and heats the contaminated MDEA solution in the flue gas treatment section to regenerate it. The combustion fuel for the furnace is supplied mostly by the PSA off-gas (~75% by mole) and any remaining required fuel is supplied by additional natural gas (~25% by mole).

Steam Pre-Reformer

Natural gas contains small amounts of higher hydrocarbons, such as ethane, propane, and butane. Coking may occur if these hydrocarbons are directly reacted at the high temperatures of the primary steam-methane reformer; thus it is preferable to let the process stream react in a low-temperature pre-reformer (operating at 783 K) prior to feeding it to the primary reformer. The pre-reformer converts approximately 80% of the ethane and essentially all of the propane and butane. A nickel-spinel ($Ni/MgAl_2O_4$) catalyst is used in the pre-reformer, which is the same as that used in the primary reformer.

Primary Steam Reformer

The primary steam-methane reformer is most of the methane is converted. The following three reactions occur simultaneously in the presence of a $Ni/MgAl_2O_4$ catalyst at a temperature of 1123 K:

$$CH_4 + H_2O = CO + 3H_2 \qquad\qquad \Delta H_1^\circ = 206.1 \text{ J/kmol} \quad (1)$$

$$CO + H_2O = CO_2 + H_2 \qquad\qquad \Delta H_2^\circ = -41.15 \text{ J/kmol} \quad (2)$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \qquad\qquad \Delta H_3^\circ = 164.9 \text{ J/kmol} \quad (3)$$

The resulting gas mixture, syngas, is rich in hydrogen and carbon monoxide. The syngas is then fed into the water-gas shift reactors to convert the carbon monoxide and recover additional hydrogen.

High-Temperature Shift Reactor

The high-temperature shift reactor is the first of the two water-gas shift reactors. In this reactor, reaction (2) occurs in the presence of a Fe_3O_4/Cr_2O_3 catalyst to convert most of the carbon monoxide to carbon dioxide and hydrogen at 623 K.

Low-Temperature Shift Reactor

The low-temperature shift reactor is the second of the two water-gas shift reactors. In this reactor, reaction (2) occurs in the presence of a Cu/ZnO catalyst to convert carbon monoxide to carbon dioxide and hydrogen at 470 K.

Flue Gas Treatment Section

In order to achieve the goal of zero carbon dioxide emissions, the flue gas must be scrubbed of carbon dioxide by an absorber. A 50% aqueous MDEA solution was selected as the absorbent, and the absorber operates at a temperature of 311 K. The cleaned gas exiting the absorber contains only 0.5% carbon dioxide by mole. The contaminated MDEA solution is regenerated by heating to 443 K, which releases all of the dissolved carbon dioxide to be sent to the dry ice production section.

MDEA Scrubber

The carbon dioxide separated by the MDEA scrubber is sent to a series of compressors to compress it to 64 atm. The high-pressure carbon dioxide is then flashed to 1 atm, which leads to rapid cooling and the solidification of most of the carbon dioxide to dry ice. The evaporated portion is recycled into the compression cycle. This allows the dry ice to be produce without the need of external refrigeration.

Pressure Swing Adsorber (PSA)

The pressure-swing adsorber uses the molecular sieve zeolite 5A to adsorb the impurities of the reactor effluents. The adsorber uses a two-hour pressure-swing cycle (one hour of adsorption and one hour of purging) and produces a product stream that is 99.9999% pure in hydrogen. 10% of the high-purity hydrogen is used to purge the adsorbent, and the released off-gas is then fed into the furnace as fuel.

The hydrogen storage system is designed to store a day's worth of hydrogen. It consists of a series of four compression stages to compress the hydrogen to 820 atm. The hydrogen is kept in 24 carbon fiber tanks that hold the hydrogen for the fueling station.

PRO/II Simulation

The process simulation software PRO/II (Invensys, Inc.) was used to model most of the unit operations and process equipment. A detailed process flow diagram that contains all of the equipment is shown in Figure 2. The following sections of this report will describe the design methodology used to determine the specifications of each process unit and present the results.
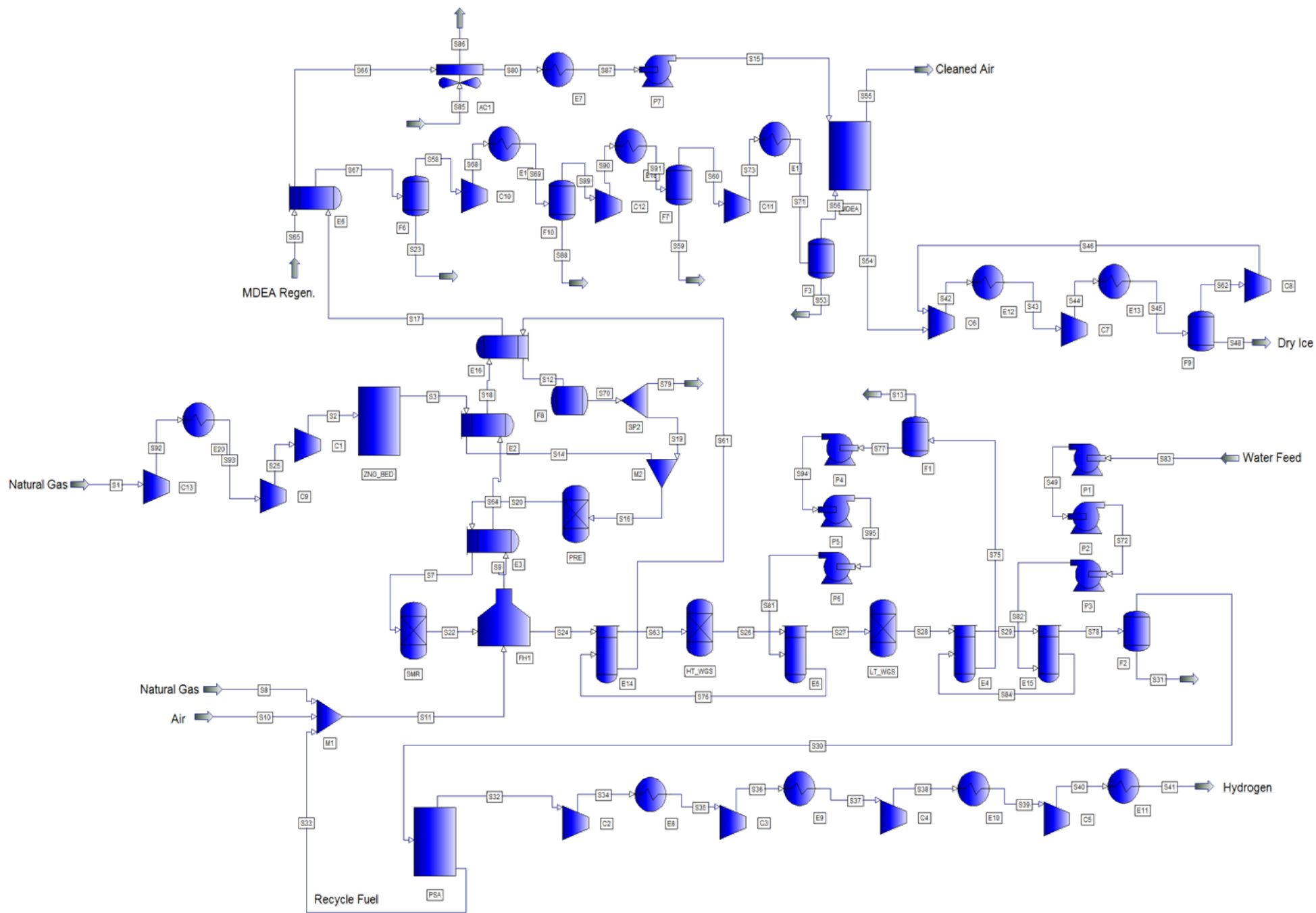
Figure 2: Process Flow Diagram

SECTION I: NATURAL GAS PROCESSING & STREAM REFORMING

Figure 3 shows the subsection of the process flow diagram that contains the equipment for natural gas processing and steam reforming. Three compressor stages and one cooler after the first stage were used to compress the natural gas from atmospheric pressure to a pressure of 30 atm. The design specifications of all compressors and heat exchangers will be discussed later in the report.
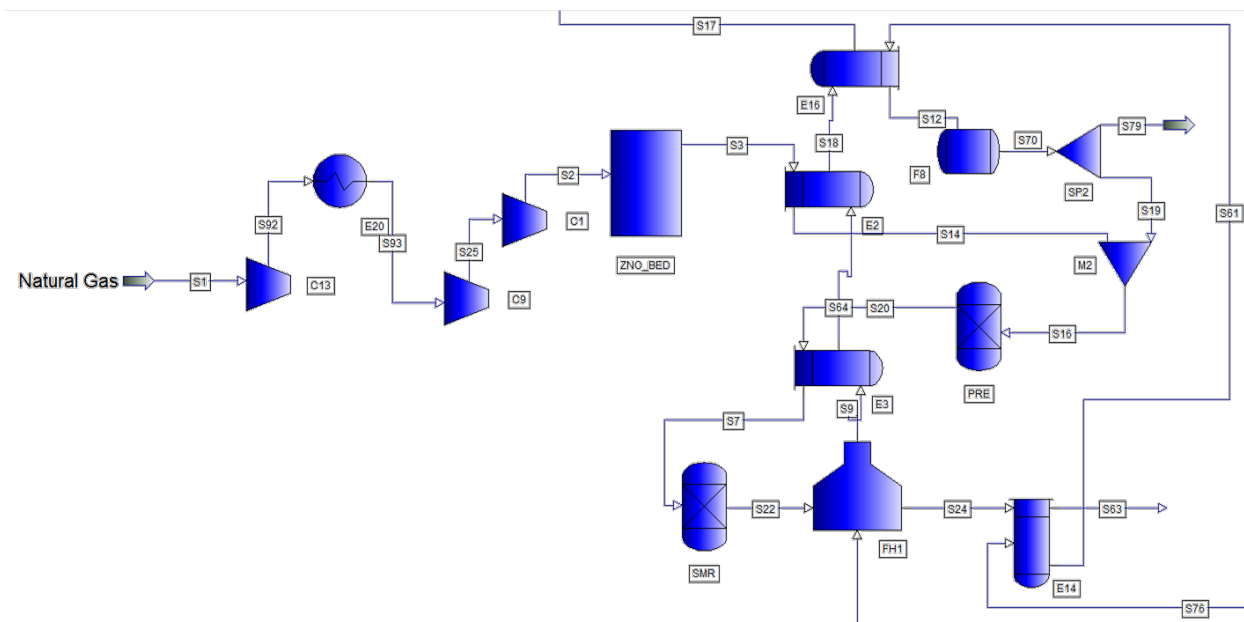
Figure 3: Natural Gas Processing & Steam Reforming

ZINC OXIDE BED

The design factors that determined the size of the ZnO bed for our plant were the amount of natural gas feedstock, the desulfurization reaction conversion efficiency, and the void fraction. The ZnO bed was sized based on an annual natural gas feedstock rate of 25,804.8 kmol/yr. This feed rate was determined previously in the overall mass balances of the H_2 production process. Given that the composition of the natural gas feedstock is 0.122 mol% H_2S, the total amount of H_2S fed to the ZnO bed is 30.65 kmol/yr. The amount of ZnO adsorbent required to remove the H_2S was determined from the stoichiometry of the following reaction:

$$H_2S + ZnO \rightarrow ZnS + H_2O$$
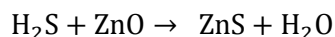
This process is essentially irreversible, allowing for complete removal of hydrogen sulfide. Assuming 100% conversion of H_2S, the total amount of ZnO required is equivalent to the amount of H_2S fed to the ZnO bed. To determine the mass of ZnO adsorbent required, the molar amount of 30.65 kmol/yr was multiplied by the molecular weight of ZnO which is 81.38 kg/kmol. The total mass of ZnO adsorbent required for complete removal of H_2S is 2,494.57 kg.

The volume and sizing of the ZnO bed was determined from the volume of adsorbent required and the void fraction. The volume of adsorbent was calculated by multiplying the mass of adsorbent by the density of ZnO which is 5606 kg/m^3. The required volume of the ZnO adsorbent is 0.445 m^3. The overall volume of the ZnO bed was determined by incorporating the void fraction. Void fraction indicates the degree of porosity of a packed bed and it is equal to the quotient of the bed bulk density and the density of a single bed particulate. The bulk density of the ZnO bed is based on the bulk density for BASF© sulfur removal beds and is equal to 1.15 g/cm^3. The density of the ZnO adsorbent particulate is equal to 5.606 g/cm^3. The void fraction of the ZnO bed is approximately 0.21 and the overall ZnO bed volume is 0.56 m^3.   The following sample calculation shows how the void fraction was calculated and consequently how the overall volume of the ZnO bed was determined:

$$\text{Bulk Density} = 1.15 \frac{\text{g}}{\text{cm}^3}$$

$$\text{ZnO Particle Density} = 5.606 \frac{\text{g}}{\text{cm}^3}$$

$$\text{Void Fraction} = \frac{\text{Bulk Density}}{\text{Particle Density}} = \frac{1.15}{5.606} = 0.21$$

$$\text{Overall ZnO Bed Volume} = \frac{\text{Volume of ZnO adsorbent}}{1 - \text{Void Fraction}} = \frac{0.445 \text{ m}^3}{1 - 0.21} = 0.56 \text{ m}^3$$

$$\text{Overall ZnO Bed Volume} = 0.56 \text{ m}^3$$

 The dimensions of the ZnO bed were based on an approximate height to diameter ratio of 2:1. The height of the ZnO bed was selected to be 1.25 m. Using the volume of the packed bed and the height of the overall unit, the diameter of the unit was calculated to be 0.76 m. The following sample calculation shows how the dimensioning of the ZnO bed was determined:

$$V = \pi r^2 h$$

$$V_{ZnO\ Bed} = 0.56\ \text{m}^3$$

$$h_{ZnO\ Bed} = 1.25\ \text{m}$$

$$r = \sqrt{\frac{V}{\pi * h}} = \sqrt{\frac{0.56\ \text{m}^3}{\pi * 1.25\ \text{m}}} = 0.38\ \text{m}$$

$$d = 2r = 2 \times 0.38\ \text{m} = 0.76\ \text{m}$$

Dimensions of ZnO bed $(h \times d)$: $1.25\ \text{m} \times 0.76\ \text{m}$

FURNACE

As mentioned earlier, the furnace is used to preheat the natural gas and steam, supply heat to the reformers, and regenerate the contaminated MDEA solution from the flue gas absorber. The furnace will have three convection banks in addition to the radiant section, as shown in Figure 4. The three convection banks from top to bottom are: the economizer, the natural gas preheater, and the primary reformer preheater.
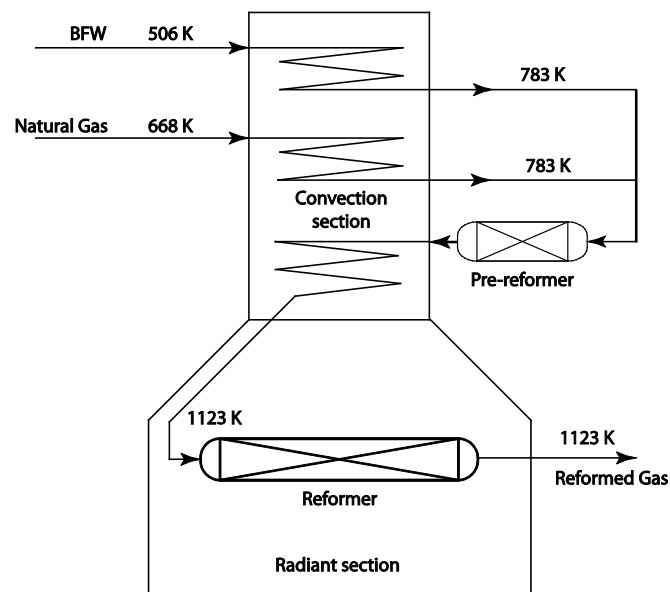
Figure 4: Diagram of furnace sections.

The convection banks[1], from top to bottom, are arranged in increasing temperature. The highest temperature operation in the furnace is the primary reformer, which will be located in the radiant section of the furnace. The furnace was modeled in PRO/II with the fired heater unit for the radiant section and a rigorous heat exchanger for each convection bank. The furnace draft is induced by downstream compressors in the flue gas processing section.

Furnace Radiant Section

Four specifications are required for the fired heater to be fully specified. Since the primary SMR should be isothermal, the process outlet temperature was set to the primary SMR's temperature of 1123 K. In addition to this specification, three assumptions were used:

1. An average tube skin temperature of 1173 K. This temperature provides a temperature difference of at least 50 K between the process side and the combustion side, but is still in the operating range of HP-45 steel.[2] For this reason, HP-45 was selected as the material for the radiant tubes as opposed to HK-40.
2. An estimated wall temperature of 1200 K.
3. 1.5% of the firing duty is lost through the wall.

The feed to the fired heater consisted mainly of PSA off-gas, which had a flow rate of 4.27 kmol/hr. From trial and error, it was determined that an additional 1.15 kmol/hr of natural gas is required to supply all of the heat for the convection banks and the MDEA regenerator. The air flow rate was maintained at an excess of 10% above the stoichiometric amount. The radiant heat transfer are was assumed to be 50% of the total tube area. Using these specifications, the remaining heat transfer properties for the radiant section were calculated by PRO/II and tabulated in Table 1.

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[1] The MDEA regenerator was not considered to be a convection bank of the furnace, but as a separate heat exchanger heated by the flue gas.

[2] Behal and Melilli, editors. (1982). *Stainless Steel Castings - STP 756*. ASTM International.

Radiant Section	
Firing Duty	464.47 kW (1.585 MMBtu/hr)
Process Duty	130.44 kW
Radiating Gas Temperature	1438.60 K
Bridgewall Temperature	1328.41 K
Tubeskin Temperature	1183.15 K
Radiant Heat Transfer Area[A]	7.16 m^2
Efficiency[B]	50%
Radiant HT Coefficient	1.58E-11 kW K^{-4} m^{-2}

Table 1: Radiant Section Properties

In order to make the SMR operate more isothermally, the heater should be top-fired such that the upper one-third length of the catalyst tubes are located closest to the burners.

Furnace Convection Section

Each convection bank was modeled as a single-pass heat exchanger in PRO/II, as seen in Table 2. The fired heater flue gas was used as the shell-side heating medium. The following tube specifications were made:

1. Tubes are of carbon steel construction.
2. Tubes have an outside diameter of 19.05 mm and a thickness of 4.216 mm.
3. Tubes are arranged triangularly with a pitch of 1 inch.
4. There are 19 fins per inch, and the fin height is 1.587 mm.

Finally, the tube-side process outlet temperature was specified for each convection bank and the simulation was allowed to converge.

The first convection bank is the economizer, which heats saturated steam at 506 K to superheated steam at 783 K. The calculated properties are listed in Table 2. The overall heat transfer coefficient was found to be 6.535 W m^{-2} K^{-1}, which is characteristic of gas-to-steam heat transfer. A total finned heat transfer area of 23.54 m^2 was found for the economizer.

Convection Bank 1 (Economizer)	
Heat Load	42.86 kW
LMTD	278.62 K
Overall Heat Transfer Coefficient	6.535 W m^{-2} K^{-1}
Efficiency	~100%
Finned Heat Transfer Area	23.54 m^2

Table 2: Economizer Heat Transfer Properties

The second convection bank is the natural gas preheater, which heats the processed natural gas from the zinc oxide bed to 783 K before it enters the pre-reformer. The calculated properties are listed in Table 3. Due to the lower required heat load, this convection bank will be the smallest, with a total finned heat transfer area of 6.78 m^2.

Convection Bank 2 (Natural Gas Preheater)	
Heat Load	13.94 kW
LMTD	364.58 K
Overall Heat Transfer Coefficient	5.638 W m^{-2} K^{-1}
Efficiency	~100%
Finned Heat Transfer Area	6.78 m^2

Table 3: Natural Gas Preheater Heat Transfer Properties

The third convection bank preheats the feed to the primary reformer to 1123 K. The heat duty also includes the additional sensible heat required by the pre-reformer, which makes this the largest convection bank. The calculated properties are listed in Table 4. The total finned heat transfer area is calculated to be 32.60 m^2.

Convection Bank 3 (Primary Reformer Preheater)	
Heat Load	87.50 kW
LMTD	270.97 K
Overall Heat Transfer Coefficient	9.905 W m^{-2} K^{-1}
Efficiency	~100%
Finned Heat Transfer Area	32.60 m^2

Table 4: Primary Reformer Heat Transfer Properties

PRE-REFORMER

The reactions in the pre-reformer are complex and are difficult to model precisely. However, holistic results were available from a study by Sperle et al. (2005), allowing the reactor product composition to

be estimated. In their studies, conversions of 3-5% for methane, 80% for ethane, and higher conversions for higher hydrocarbons were observed.[3] To model the pre-reformer, a set of reactions was defined in PRO/II with the conversions listed in Table 5.

Reaction	Conversion
$CH_4 + H_2O = CO + 3H_2$	4%
$C_2H_6 + 2H_2O = 2CO + 5H_2$	85%
$C_3H_8 + 3H_2O = 3CO + 7H_2$	95%
$C_nH_m + nH_2O = nCO + \left(n + \frac{m}{2}\right)H_2;$ $n \geq 4$	100%

Table 5: Pre-Reformer Conversions

The reactor was modeled adiabatically, which is similar to the conditions in which it will be operating. A steam to natural gas ratio of 4 was used to reduce the risk of coking in both the pre-reformer and later in the primary reformer. The outlet temperature was calculated in PRO/II. The operating conditions are summarized in Table 6.

Inlet Stream	Steam and processed natural gas, 4 to 1 ratio by mole
Outlet Stream	Pre-reformed gas
Temperature	783 K (inlet)
	693 K (outlet)
Pressure	29 atm

Table 6: Pre-Reformer Operating Conditions

The pre-reformer size is assumed to be equivalent to the heat transfer area required to raise the temperature of the pre-reformed gas to the primary reformer temperature of 1123 K. This calculation will be shown in the furnace design description. A more detailed calculation with a kinetic model may be required to determine if the size of the pre-reformer will be reaction-limited or heat-transfer limited.

PRIMARY STEAM-METHANE REFORMER (SMR)

Xu and Forment's kinetic equations for steam-methane reforming were used to model the reformer.[4] A reactor model was written in MATLAB[5] and used to find the residence time required to achieve a

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[3] Sperle et al., 2005

[4] Xu and Froment, 1989

[5] See Listings 1 to 5 in Appendix A for the script and all subroutines used.

reasonable conversion in isothermal conditions. The feed composition and rate were taken from the outlet stream of the pre-reformer modeled in PRO/II. It was decided with trial and error that 200 kg of Ni/MgAl$_2$O$_4$ catalyst should be used in the SMR in order to achieve a reasonable residence time. The resulting plot of component molar flow rate as a function of residence time is shown in Figure 5.
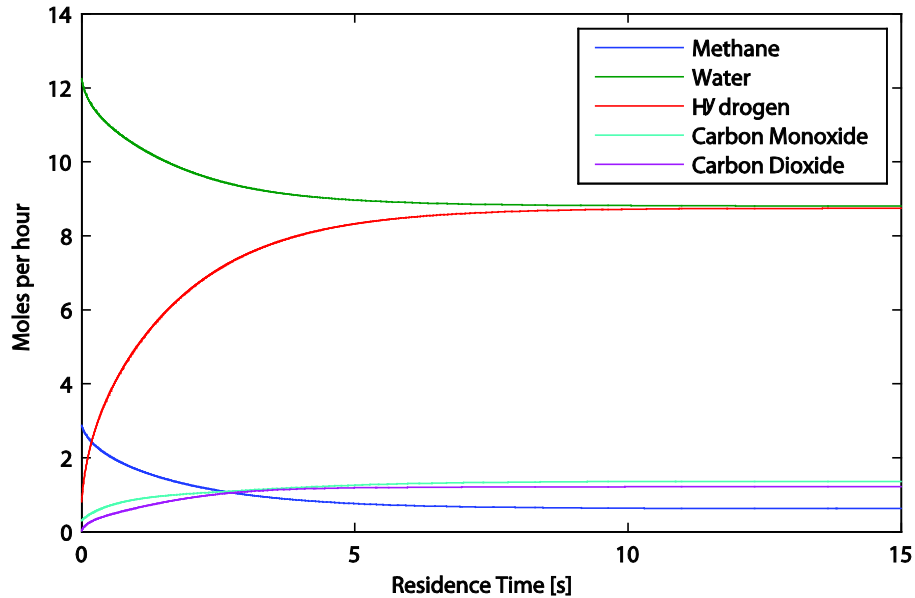
Figure 5: Plot of Component Molar Flow Rates as a Function of Residence Time

It can be seen that the reactor approaches equilibrium within 15 seconds of residence time. In order to model the reactor in PRO/II, the reactions were treated as if they proceeded in series, with reaction (1) followed by reaction (2). Reaction (3) was excluded in this treatment because it is simply the sum of reactions (1) and (2). The effective conversion was calculated in terms of reactions (1) and (2) with the following formulas:

$$X_1 = 1 - \frac{n_{CH_4,out}}{n_{CH_4,in}}$$

$$X_2 = 1 - \frac{n_{CO,out}}{n_{CH_4,in} - n_{CH_4,out} + n_{CO,in}}$$

The effective conversions were found to be 77.9% for reaction (1) and 46.7% for reaction (2). These values were specified as extents of reaction in a PRO/II conversion reactor, with the multiple conversion

basis set to "reaction." The PRO/II model produced the same result as that predicted by the MATLAB model, with 42% hydrogen by mole in the product stream.

The amount of required tubing was calculated based on the residence time, void fraction, and volumetric flow rate. First, the volume of gas in the reactor was calculated:

$$V_{gas} = \frac{\dot{V}}{\tau}$$

$$V_{gas} = \frac{\left(53.6 \frac{m^3}{hr}\right) * \left(\frac{1 \text{ hr}}{3600 \text{ s}}\right)}{15 \text{ s}}$$

$$V_{gas} = 0.223 \text{ m}^3$$

Given a void fraction of $\varepsilon = 0.528$ for $Ni/MgAl_2O_4$ catalyst[6], the total reactor volume could then be calculated:

$$V_{total} = \frac{V_{gas}}{\varepsilon}$$

$$V_{total} = 0.432 \text{ m}^3$$

For tubes with an outer diameter of 130 mm and a thickness of 12.5 mm, it was determined that a total length of 48.8 m would be required.

$$\text{Length of reactor} = \frac{V_{total}}{\pi \left(\frac{OD - \text{Thickness}}{2}\right)^2}$$

$$\text{Length of reactor} = 48.8 \text{ m}$$

In order to determine the layout of the reformer tubes in the furnace, a plot of heat duty per unit length along the reactor was generated (see Listing 1 in Appendix A). From Figure 6, it is evident that the most heat duty is required in the first 10 meters of the reactor. Thus, the entry point of the reactor should be

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[6] Xu and Froment, 1989

located near the furnace burners to increase the heat flux in that portion and promote isothermal operation. The design of the furnace is discussed in more detail in the next section.
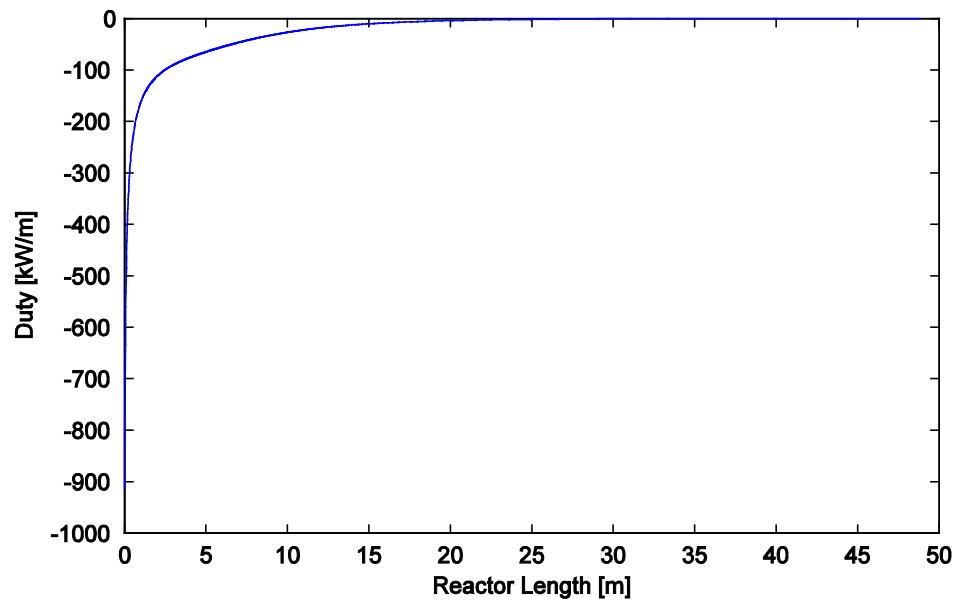
Figure 6: Heating Duty along Length of Reactor

SECTION II: WATER GAS SHIFT

Figure 7 shows the water-gas shift section, which includes both the HTS and LTS reactors. This section is also where most of the heat integration takes place, since the water to be fed into the reformer is used as coolant for the water-gas shift reactors. The design of the pumps and heat exchangers are described in their respective sections.

Figure 7: Water Gas Shift Section

HIGH-TEMPERATURE SHIFT REACTOR (HTS)

The HTS reactor converts most of the carbon monoxide in the syngas to carbon dioxide and produces additional hydrogen. The kinetic equation for reaction (2) over Fe_3O_4/Cr_2O_3 catalyst was provided by Keiski et al. (1995).[7] The reactor was first modeled in MATLAB to determine the required residence time. The script and subroutines are available in Listings 7 to 9 in Appendix A. A plot of component molar rates as a function of residence time is shown in Figure 8 for a reactor containing 300 kg of catalyst. It can be seen that the reactor essentially reaches equilibrium within 15 seconds.

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[7] Keiski et al., 1995

Figure 8: HTSR Component Molar Flow Rates as a Function of Residence Time

The HTS reactor was also modeled in PRO/II as an equilibrium reactor. The reactor was specified to operate isothermally at 623 K, and the built-in water-gas shift reaction set was used to model the conversion. PRO/II calculated the heat duty of the reactor to be 12.56 kW.

In terms of the physical design, the reactor will be a fixed-bed reactor with cooling water on the shell side. The amount of cooling water required could be calculated from the heat duty:

$$\dot{m}_{CW} = \frac{Q}{\left(T_{CW,out} - T_{CW,in}\right)C_p}$$

$$\dot{m}_{CW} = \frac{12.56 \text{ kW}}{(353 \text{ K} - 298 \text{ K}) * (4.1868 \text{ kJ K}^{-1} \text{ kg}^{-1})}$$

$$\dot{m}_{CW} = 0.0545 \text{ kg/s}$$

$$\dot{m}_{CW} = 196.29 \text{ kg/hr}$$

The total tube length of the HTS reactor was calculated in the same manner as the SMR tube length was. Assuming a catalyst void fraction of 0.5 and reactor tubes with 130 mm OD, the tube length required is 37.9 m.

LOW-TEMPERATURE SHIFT REACTOR (LTS)

The LTS reactor converts some of the remaining carbon monoxide in the HTS product stream to recover additional hydrogen. The kinetic equation for reaction (2) over a Cu-ZnO catalyst was provided by Rase (1991).[8] The reactor was first modeled in MATLAB to determine the required residence time. The script and subroutines are available in Listings 10 to 12 in Appendix A. A plot of component molar rates as a function of residence time is shown in Figure 9 for a reactor containing 300 kg of catalyst. Like the HTS reactor, this reactor also reaches an equilibrium within 15 seconds.
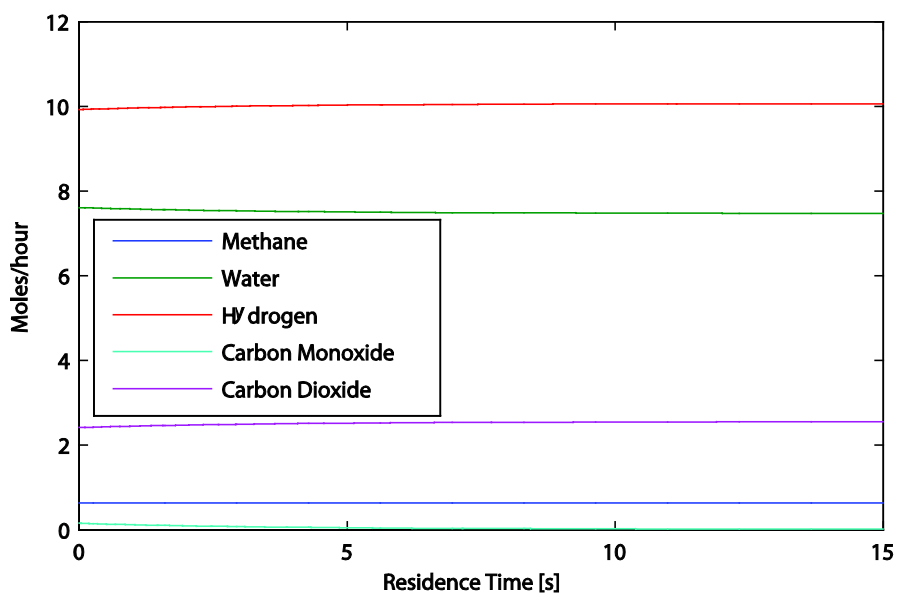
Figure 9: LTSR Component Molar Flow Rates as a Function of Residence Time

The LTS reactor was also modeled in PRO/II as an equilibrium reactor. The reactor was specified to operate isothermally at 470 K, and the built-in water-gas shift reaction set was used to model the conversion. PRO/II calculated the heat duty of the reactor to be 1.428 kW.

In terms of the physical design, the reactor will be a fixed-bed reactor with cooling water on the shell side. The amount of cooling water required could be calculated from the heat duty:

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[8] Rase, 1991

$$\dot{m}_{CW} = \frac{Q}{(T_{CW,out} - T_{CW,in})C_p}$$

$$\dot{m}_{CW} = \frac{1.428 \text{ kW}}{(353 \text{ K} - 298 \text{ K}) * (4.1868 \text{ kJ K}^{-1} \text{ kg}^{-1})}$$

$$\dot{m}_{CW} = 0.00619 \text{ kg/s}$$

$$\dot{m}_{CW} = 22.29 \text{ kg/hr}$$

The total tube length of the LTS reactor was calculated in the same manner as the SMR and HTS tube length were. Assuming a catalyst void fraction of 0.5 and reactor tubes with 130 mm OD, the tube length required is 37.9 m.

SECTION III: FLUE GAS TREATMENT
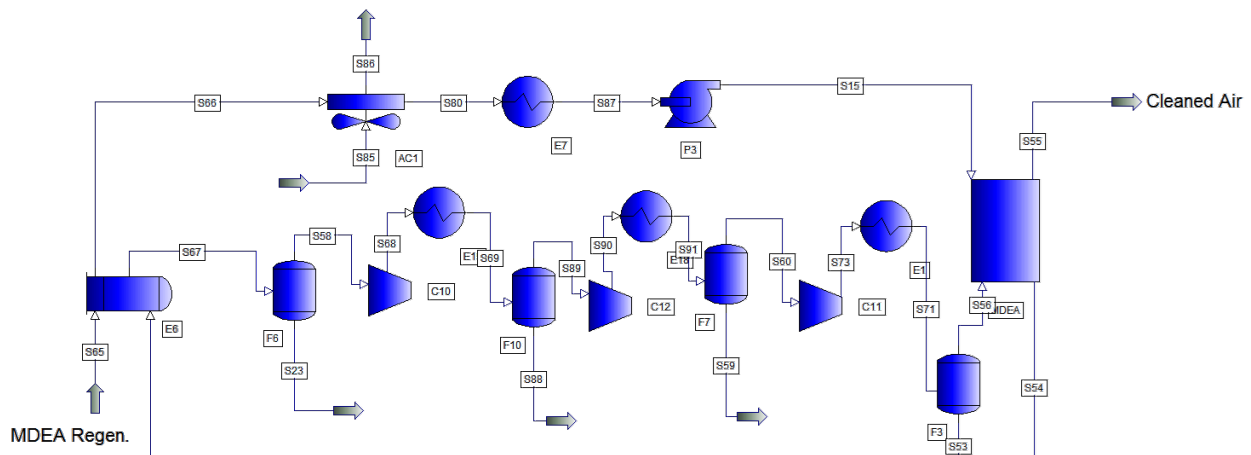
Figure 10: Flue Gas Treatment

MDEA SCRUBBER

MDEA was selected as the absorbent because of its low heat of absorption and well-documented equilibrium characteristics. The equilibrium model for the CO_2 solubility in MDEA was provided by Posey et al. (1996).[9] The McCabe-Thiele graphical method was used to determine the number of equilibrium stages required (see Listing 13 for script). The following design specifications were chosen:

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[9] Posey et al., 1996

1) A design operating temperature of 311 K was chosen such that the absorber will be able to operate at ambient temperatures.

2) Since absorption occurs better at higher pressures, an operating pressure of 16 atm was chosen.

3) A liquid flow rate of 21 kmol/hr 50% MDEA solution was selected.

4) The emitted gas was allowed to contain 0.5% carbon dioxide by mole.

Figure 11 shows the resulting equilibrium curve and operating line with these specifications. The McCabe-Thiele method, which is used to determine the number of stages, predicted five theoretical stages for the absorber.
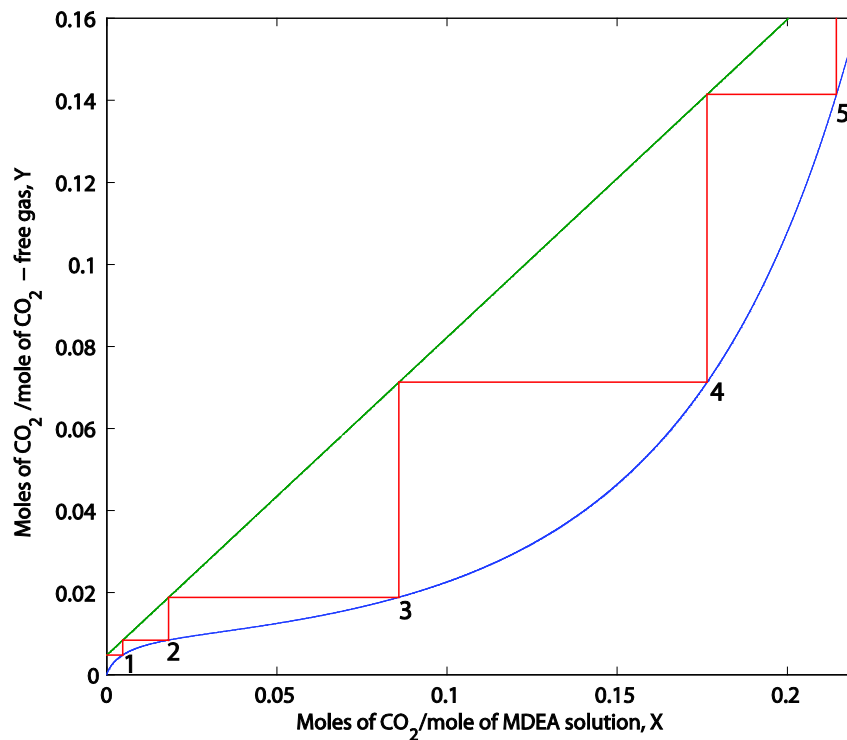
Figure 11: McCabe-Thiele Graph for MDEA Scrubber

Due to the relatively small flow rate of gas to be cleaned, the absorber was designed as a packed column. 16 mm steel Pall Rings were chosen as the packing since they were the least expensive option

and only five theoretical stages were required. For Pall Rings, the following correlations were available to determine the height of a theoretical plate (HETP):[10]

$$a_p = \frac{5.2}{D_p} = \frac{5.2}{0.016\ m} = 325\ m^2/m^3$$

$$HETP = \frac{93}{a_p} = \frac{93}{325\ m^2/m^3} = 0.286\ m$$

A diameter of 0.2 m was chosen, from which the pressure drop could be estimated. The superficial gas velocity, U_s, flow parameter, F_{LV}, were found as follows:

$$U_s = \left(\frac{V_{mass}}{\rho_V}\right)\left(\frac{\pi D_t^2}{4}\right)^{-1}$$

$$= \left(\frac{825.732\ \frac{kg}{hr}}{19.175\ \frac{kg}{m^3}}\right)\left(\frac{\pi(0.2)^2}{4}\right)^{-1}$$

$$= 1370.74\ \frac{m}{hr}$$

$$= 1.249\ \frac{ft}{s}$$

$$F_{LV} = \left(\frac{L_{mass}}{V_{mass}}\right)\left(\frac{\rho_V}{\rho_L}\right)$$

$$= \left(\frac{1440.38}{825.73}\right)\left(\frac{19.175}{1017.49}\right)$$

$$= 0.239$$

The capacity factor, C_p, was then calculated, using a packing factor of $F_P = 78\ ft^{-1}$ for 16 mm Pall Rings and the kinematic viscosity of 11.05 centistokes for the MDEA solution.

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[10] Green and Perry, 2008

$$C_p = U_s \left(\frac{\rho_V}{\rho_L - \rho_V} \right)^{0.5} F_P^{0.5} \nu^{0.5}$$

$$= \left(1.249 \frac{\text{ft}}{\text{s}} \right) \left(\frac{19.175}{1017.49 - 19.175} \right)^{0.5} (78 \text{ ft}^{-1})^{0.5} (11.05 \text{ cSt})^{0.5}$$

$$= 1.72$$

From Eckert's generalized pressure drop correlation[11], the pressure drop was found to be approximately 2.5 inches of water per foot of packing height, or 2 kPa per meter of packing. With a packing height of 1.4 m, the pressure drop through the absorber is only 2.9 kPa, or 0.029 atm. The specifications and calculated properties of the absorber are summarized in Table 7.

MDEA absorber	
No. of theoretical stages	5
Packing Type	16 mm Pall Rings
HETP	0.286 m
Column Height	1.43 m
Column Diameter	0.2 m
Pressure Drop	2.9 kPa
MDEA flow rate	21 kmol/hr
Flue gas	

Table 7: MDEA Absorber Properties

MDEA REGENERATOR

The MDEA regenerator heats the contaminated MDEA to release the absorbed carbon dioxide such that the MDEA can be recycled back to the absorber. A temperature of 443.15 K was selected for the regenerator, which allows the carbon dioxide to be released without depressurizing the solution. The equilibrium amount of dissolved carbon dioxide in the MDEA solution at this temperature was determined to be 0.036% by mole (see Listing 14 in Appendix A for calculation script). A heat exchanger was modeled in PRO/II with 21 kmol/hr of 50% MDEA solution in the tube side to design the heat exchanger required for regenerating the MDEA. The carbon dioxide stripped from the MDEA solution enters the dry ice production section, while the regenerated MDEA is cooled and reactivated with an air-

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[11] Green and Perry, 2008

cooled heat exchanger. The specifications of the heat exchange equipment are available in its respective section.

SECTION IV: DRY ICE PRODUCTION

This section of the process consists of an auto refrigeration cycle that is comprised of two heat exchangers, three compressors and a dry ice flash tank. The heat exchangers act as after coolers for the carbon dioxide, which must be compressed and cooled to produce dry ice. The design for these heat exchangers and compressors are specified below in Table 14 and Table 16, respectively. The design of the dry ice flash tank is shown below; the specifications for this flash tank are listed in Table 18. In this process, approximately 12.227 kmol/hr of the carbon dioxide rich flue gas is recycled back to the first compressor while 4.289 kmol/hr is compressed and sold as dry ice.
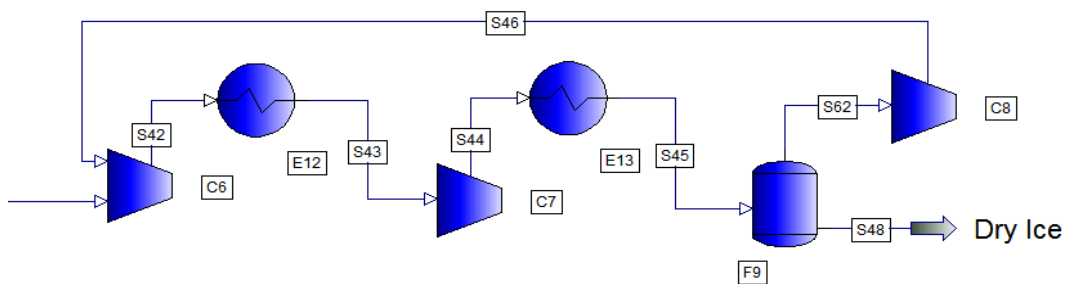
Figure 12: Dry Ice Production

SECTION V: PRODUCT PROCESSING

The hydrogen-rich stream coming from the water gas shift reactors must be purified and compressed to the desired product requirements. The purification occurs by passing the stream through a pressure swing adsorber. The design for this separation units is shown below and the design specification are listed in Table 10. There is a 10% recycle of hydrogen product fed back to the PSA to regenerate the adsorbent. The starting pressure of the stream before entering the series of compressors is 17 atm and the final product pressure is 821 atm. The system consists of 4 heat exchangers and 4 compressors; the specifications for these units are listed in Table 15 and Table 16, respectively.
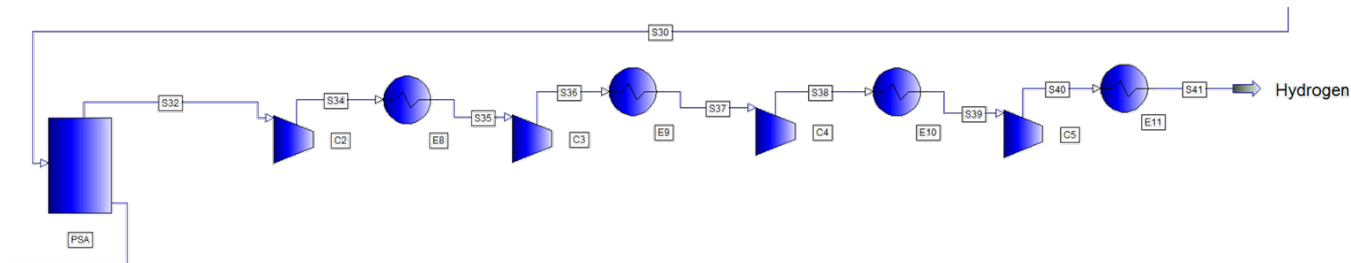
Figure 13: Hydrogen Product Processing

PRESSURE-SWING ADSORBER (PSA)

The pressure swing adsorber is designed with two beds connected in parallel. The pressure swing adsorber is designed such that it runs on a two-hour cycle. During the first hour, one bed is adsorbing while the other is desorbing and during the second hour, the beds switch modes of operation. Thus, the beds were designed such that at the end of the hour, maximum loading is reached. The chosen adsorbent was UNIMOL 5A zeolite, which is a calcium-sodium based molecular sieve adsorbent with spherical geometry. This adsorbent has a 5-year lifetime. The properties of this adsorbent are listed below in Table 8.

5A Molecular Sieve Zeolite	
Bulk Density (g/mL)	0.66
Critical Diameter (A)	5
Particle Diameter (mm)	2
Wear Ratio (%)	0.2
Crushing Strength (per piece)	60
Static Water Adsorption (%)	21.5
Void Fraction	0.47
Regeneration Method	Decrease P
Moisture Removal Method	Decrease T (250-300 °C)

Table 8: Adsorbent Properties

The pressure swing adsorber is designed to remove enough carbon dioxide such that the final hydrogen purity is 99.9999%. The purge stream is purified hydrogen; approximately 10% of the final product is recycled to the pressure swing adsorber to purge the bed and regenerate the adsorbent. Table 9 shows the properties of all streams leaving and exiting the PSA.

Stream Properties		
Feed Properties	CO_2 Composition	0.191
	H_2 Composition	0.75
	Flow Rate (lbmol/hr)	41.82
	Flow Rate CO2 (lbmol/hr)	8
Purge Stream	CO_2 Removed (g/100 g adsorbent)	0.8998
	H_2 Composition	99.9999%
	Flow Rate (lbmol/hr)	2.84
Hydrogen Product Stream	H_2 Composition	99.9999%
	Flow Rate (lbmol/hr)	25.52
Off-Gas	CO_2 Composition	0.11
	Flow Rate (lbmol/hr)	0.74

Table 9: PSA Stream Properties

The feed stream properties were provided by PRO/II. From this, since the carbon dioxide content was known; in order to reach the desired hydrogen purity, the amount of carbon dioxide needed to be removed was also determined. On an hourly basis, the total amount of adsorbent required, assuming max loading at 311 K, was calculated. From the weight of the adsorbent, the total volume required was calculated. From the total volume, the volume of the adsorber was calculated. Table 10 shows the design specification for the pressure swing adsorber that will operate over 2-hour cycles.

Design Specifications	
Carbon Dioxide Weight (g)	159623
Weight Adsorbent (g)	17736
Volume Adsorbent (m^3)	0.27
Adsorber Volume (m^3)	0.3

Table 10: PSA Design Specifications

DESIGN OF HEAT EXCHANGERS

PRO/II was used to obtain the necessary data for the design of heat exchangers. Heat exchangers were designed to follow a shell and tube model. Most heat exchangers when modeled in PRO/II were entered as simple heat exchangers. For the simple heat exchangers, PRO/II is capable of outputting the heat loads (Q) and the log mean temperature difference (LMTD). The overall heat transfer coefficients

(U) were estimated using a chemical engineering online resource.[12] The heat transfer coefficient estimates were based on the temperature differences, the heat loads, the material (chosen to be carbon steel), and most importantly, the phases of the streams on the shell and tube sides. For the following sections, a rigorous heat exchanger design was implemented in PRO/II: the MDEA regenerator, the MDEA air cooler, the furnace convection bank, and the syn-gas treatment heat exchanger. Rigorous heat exchangers will also output the overall heat transfer coefficient (U) along with the heat load and the log mean temperature difference. In order to find the heat exchange area, the following equation was used:

$$Q = UA\Delta T_{lm}$$

The following tables show the PRO/II values for the temperature differences and heat loads, the heat transfer coefficients (either estimated or obtained from PRO/II depending on type of heat exchanger used), and the calculated areas. Once the initial area estimate was determined, a 25% adjustment was made for each of the heat exchange areas. The areas listed below showed the design (corrected) areas.

HEX	Description	LMTD (K)	Heat Transfer Coefficient (U- W/m^2 K)	Heat Load (W)	Area (m^2)
2	Natural gas feed preheater	350.585	10	14816.67	8.475
3	Primary reformer preheater	258.191	10	87500	67.8
21	Steam Superheater	257.417	20	42777.8	16.625
20	Natural gas compressor after-cooler	46.486	30	5247.2	7.55

Table 11: Natural Gas Pretreatment & Steam Reformation Heat Exchangers

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[12] Schlünder, 1993

HEX	Description	LMTD (K)	Heat Transfer Coefficient (U- W/m² K)	Heat Load (W)	Area (m²)
14	Reformer exit stream cooler	300.948	30	106111.1	23.525
15	Reactant water condenser	16.006	50	12741.67	31.85
5	HT to LT cooler	77.337	30	31388.89	27.075
4	Reactant water condenser	9.302	374	105722.2	60.8

Table 12: Water Gas Shift Heat Exchangers

HEX	Description	LMTD (K)	Heat Transfer Coefficient (U- W/m² K)	Heat Load (W)	Area (m²)
1	Flue gas compressor after-cooler	39.742	30	31111.11	52.2
7	MDEA Reactivator	12.343	900	154722.2	27.875
AC1	MDEA Reactivator (Air-cooled)	46.679	5.52	144938.9	562.782
17	MDEA Regenerator	102.685	30	154722.2	100.475
18	CO2 compressor after-cooler	54.128	30	52500	64.675
19	Flue gas compressor after-cooler	43.136	30	36388.89	56.25

Table 13: Flue Gas Treatment Heat Exchangers

HEX	Description	LMTD (K)	Heat Transfer Coefficient (U- W/m^2 K)	Heat Load (W)	Area (m^2)
12	CO2 compressor after-cooler	36.259	30	21533.3	39.6
13	CO2 compressor after-cooler	45.595	30	35833.3	52.4

Table 14: Dry Ice Production Heat Exchangers

HEX	Description	LMTD (K)	Heat Transfer Coefficient (U- W/m^2 K)	Heat Load (W)	Area (m^2)
14	Reformer exit stream cooler	300.948	30	106111.1	23.525
15	Reactant water condenser	16.006	50	12741.67	31.85
5	HT to LT cooler	77.337	30	31388.89	27.075
4	Reactant water condenser	9.302	374	105722.2	60.8

Table 15: Hydrogen Product Processing Heat Exchangers

The heat exchangers designed up show all areas except for those of heat exchangers belong to the convection section of the furnace. These three heat exchangers were designed above in the furnace section of the report.

DESIGN OF COMPRESSORS

Comp	Work (kW)	HP	Inlet T (K)	Outlet T (K)	Inlet Pressure (atm)	Outlet Pressure (atm)	Compression Ratio	Compressor Type
1	3.7807	5.07	401.4	499.9496	12.2474	30	2.5	Centrifugal
13	5.6653	7.6	298.15	459.53	1	5	5	OFS
9	2.9789	3.99	313	401.402	5	12.2474	2.5	OFS
2	9.38	12.58	311	437.53	21	52.5	2.5	Centrifugal
3	9.68	12.98	313	441.16	52.5	131.25	2.5	Centrifugal
4	10.32	13.84	313	443.13	131.25	328.12	2.5	Centrifugal
5	12.03	16.13	313	447.9	328.12	820.31	3	Reciprocating
6	23.19	31.1	291.47	425.33	4	16	4	OFS
7	23.78	31.893	313	456.43	16	64	4	Centrifugal
8	11.32	15.18	185.13	288.75	1	4	4	OFS
10	26.22	35.16	321.24	432.78	1	2.4	2.5	OFS
11	29.02	38.92	309.99	448.52	5.6	16.35	3	OFS
12	28.98	38.86	307.56	443.69	2.05	5.95	3	OFS

Table 16: Compressor Design Specifications

The entire process requires 13 pumps; these are listed above in Table 16. This table also specifies the operating conditions of each compressor and the final design chosen. The design of the compressor was chosen based on the data compiled in Table 2: How the four basic types of compressors stack up in Jandjel's paper *Select the Right Compressor*.[13] The important factors considered were the maximum outlet pressure, the maximum temperature, and the compression ratio.

DESIGN OF PUMPS

Pumps with a head greater than or equal to 20 meters were considered in the design process. The following pumps are in series and are located in the water gas shift section of the process; the initial pressure of the process stream entering the first compressor is 1 atm and the final pressure leaving the third compressor is 5 atm. The work done by pump is extremely small, which allowed for the use of reciprocating pumps. The design chosen was based also on the net positive suction head (NPSH) and the pressures. The inlet pressures, work values, and efficiencies were determined using the original design schematic as well as PRO/II. PRO/II outputs also contained the NPSH values; the calculated NPSH values were compared with the PRO/II output values.

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[13] Gregory, 2000

Pump	Inlet P (atm)	Max ΔP (atm)	Outlet P (atm)	NPSH$_{act}$ (m)	NPSH$_{PRO/II}$ (m)	W (kW)	η$_{adiabatic}$	W$_{actual}$ (kW)	Design
1	1	0.97	1.9	10.04	9.34	0.12	0.77	0.2	Reciprocating
2	1.9	1.87	3.45	19.37	16.07	0.04	0.77	0.1	Reciprocating
3	3.45	3.42	5	35.43	16.08	0.07	0.77	0.1	Reciprocating

Table 17: Pump Design Specifications

The vapor pressure of water at atmospheric conditions (P$_{vapor}$), from literature, is 0.031 atm. In order to find the NPSH, the following relationship was used:

$$NPSH = \Delta P_{max} \times \frac{101325\ Pa}{atm} \times \frac{0.000102\ m}{Pa}$$

$$\Delta P = P_{inlet} - P_{vapor}$$

The outlet pressure was determined from the following relationship:

$$P_{outlet} = P_{inlet} + \Delta P_{max}$$

For pumps 1 and 2, the calculated NPSH values compare relatively well to the PRO/II NPSH values. However, for pump 3, the calculated value was significantly higher than the PRO/II value. The larger value was used because overdesign is always preferred.

DESIGN OF TANKS

Dry Ice Flash Tank

A flash tank was also designed for the dry ice section. The design pressure and the flowrate were obtained from PRO/II. The diameter was chosen to be 0.2 and the height was calculated accordingly. The maximum stress was set at 10800 psi and the design thickness was a rounded manufacturer's value based on the calculated thickness.

Specification		Dry Ice
Design Pressure (psi)	P_{design}	30
Flowrate (m^3/hr)	F	0.248
Liquid Holdup	s	30
Level (%)	L	25
Volume (m^3)	V	0.0083
Diameter (m)	D	0.2
Radius (m)	R	0.1
Height (m)	H	0.26
Head Surface Area (m^2)	HAS	0.13
Maximum Stress (psi)	S_{max}	10800
Thickness (in)	t	0.16
Design Thickness (m)	t_{design}	0.013
Shell Volume (m^3)	V_{shell}	0.003
Shell Weight (kg)	W	21.5

Table 18: Dry Ice Flash Tank Specifications

The following series equations represent the design relations used to determine the specifications of the dry ice flash tank. The calculated design specifications for the dry ice flash tank are listed above in Table 18.

$$V = \frac{sF}{L}$$

$$H = \frac{V}{\frac{D^2 \pi}{4}}$$

$$HSA = 4\pi R^2$$

$$t = \frac{P_{design}(R)}{S_{max} - 0.6P_{design}}$$

$$V_{shell} = (2\pi RH + HSA)t_{design}$$

$$W = 7850V_{shell}$$

Product Storage Tanks

Storage tanks were designed to hold up to 400 kg of hydrogen, which is the demand for one day. This allows a 24-hour shut down period per year. This was the chosen design because of the high cost of high pressure storage vessels. The number of tanks used was chosen to be 24 and the diameter was also estimated.

Hydrogen Storage Specifications		
Storage Capacity (kg)	C	400
Storage Pressure (psi)	P	83118
Storage Temperature (K)	T	313
Volume (m³)	V	12.52
Number of Tanks	N	24
Unit Volume (m³)	V_{unit}	0.52
Diameter (m)	D	0.63
Radius (m)	R	0.315
Length (m)	L	1.67
Aspect Ratio	L:D	2.66

$$V = \frac{8.314472CT}{P}$$

$$V_{unit} = \frac{V}{24}$$

$$L = \frac{V}{\frac{D^2\pi}{4}}$$

$$Aspect\ Ratio = \frac{L}{D}$$

HEAT & UTILITIES INTEGRATION

Pinch Analysis

In order to save on utilities, pinch analysis was performed on the plant to find candidate streams for cooling and heating. Pinch analysis is the method that is used during the heat and utility integration stage of the process design. It is used to minimize energy consumption when designing a chemical process. A pinch analysis can be used to determine where feasible amounts of energy can be recovered and use in other areas of the process where energy is required.

Cold Streams	
T (K)	ΔH (kW)
311	176.9946
353.15	226.1961
368.35	250.9091
503.79	313.0164
667.92	422.8033
692.93	440.8656
783.15	524.3719
1123.15	665.039

Table 19: Pinch Analysis Energy & Heat Data (Cold Streams)

Hot Streams	
T (K)	ΔH (kW)
311	0
313	2.334633
368.349	154.5469
425.69	245.3021
437.53	261.5317
441.16	266.2436
443.13	268.6446
447.9	273.9168
456.43	282.6981
470	292.9361
623.15	324.325
1123.15	430.4361

Table 20: Pinch Analysis Energy & Heat Data (Hot Streams)
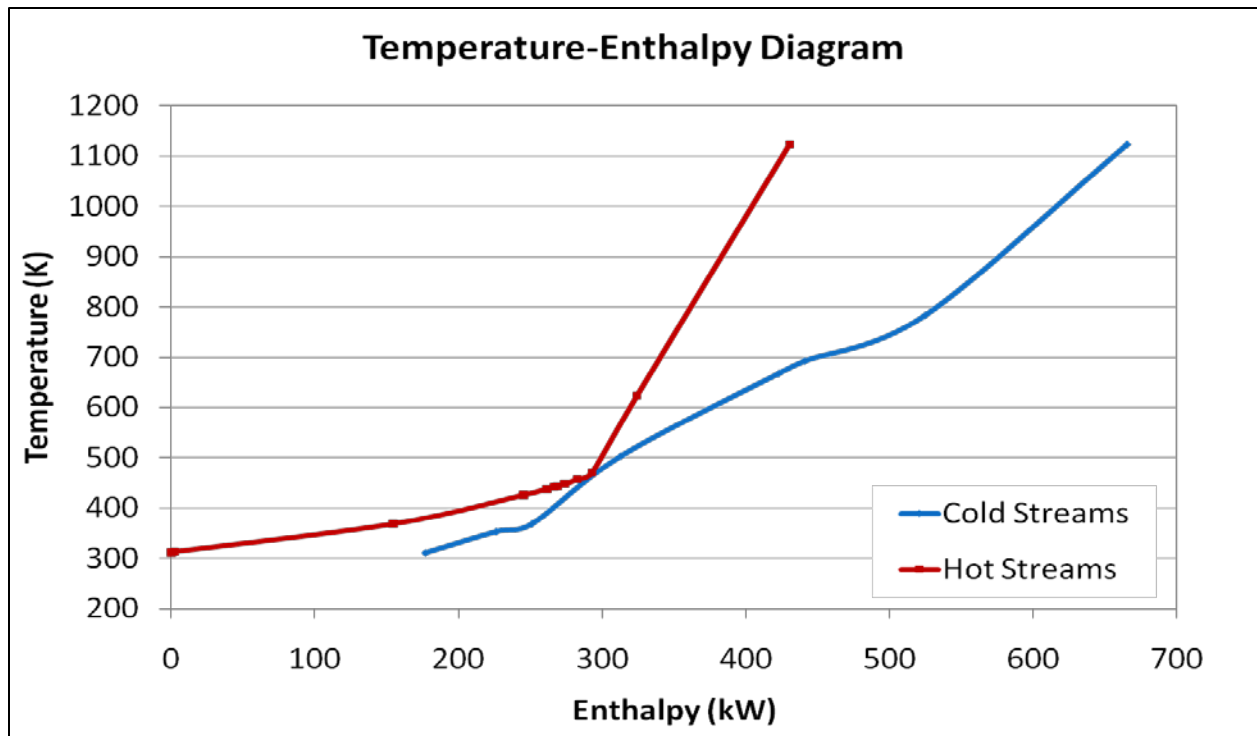
Figure 14: Pinch Analysis Curve (Temperature vs. Enthalpy)

Energy flow data is obtained as a function of the heat load on a particular stream. The data was obtained from PRO/II and plotted to form composite hot and cold curves. The hot curves are plotted from the streams that are releasing heat and the cold curves are plotted from the streams that are taking in heat. The point at which, the cold and hot streams are closest is called the pinch temperature. The pinch temperature occurs at the low-temperature water gas shift reactor product stream of 470 Kelvin. From this, heat exchanges can be matched; a hot stream with a temperature above the pinch point is matched with a cold stream with a temperature below the pinch point. This reduces the heat exchanger requirements, allows energy to be obtained from within the process, and ultimately, reduced energy usage and costs. From Figure 14, it is clear that the reactor product streams are good candidates for heat recovery. This heat was recovered by using it to boil feed water.

COST ANALYSIS

The cost analysis included an in-depth study of each component included in the plant. Initial estimates of equipment and utility costs allowed for further evaluation of the process to minimize utility usage and equipment sizes. Three different costing protocols were used and compared in order to determine best estimates for installed equipment costs.

SEPARATION UNIT & REACTOR COSTS

The following cost estimates were obtained using Matche (a chemical engineering cost estimating resource)[14]. Presented below in Table 21 are roughly estimated bare module costs for each of the separation units and reactors. The chosen material for these reactors was carbon steel except for the convection section of the furnace, which uses HP-45 alloy, which is a steel based material). The furnace cost includes both the steam reforming reactors as well as the heat exchangers required for the convection bank. This explains the large cost associated with this section. The costs obtained from the resource were then adjusted from the 2007 CEPCI (525.4) value to the 2010 CEPCI value (558.2).

Unit	Cost
ZnO Bed	19,500
MDEA Absorber	15,100
MDEA Stripper	13,400
Pressure Swing Adsorber (2)	71,800
Furnace, Pre-Reformer, Primary Reformer	331,700
High-Temperature Shift Reactor	99,900
Low-Temperature Shift Reactor	99,900

Table 21: Separation Units and Reactor Costs

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[14] Matches < http://www.matche.com/EquipCost/index.htm>

The highest costs are due to the furnace, steam reforming, and the water-gas shift reactions. This is a reasonable investment due to the operating temperature and pressures of these components.

<div align="center">

HEAT EXCHANGER COSTS

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After completing the heat integration, the heat exchangers were designed and costed. The chosen material for the heat exchangers for the design temperatures, pressures, and enthalpy is carbon steel. The purchase costs for each shell and tube heat exchanger in our plant's heat exchange network were determined using the following empirical purchase cost equation[15]:

$$C_P = F_P \times F_M \times F_L \times C_B$$

C_P represents the purchase cost of heat exchanger in dollars, F_P represents a unitless pressure factor, F_M represents a unitless materials factor, F_L represents a unitless tube-length correction factor, and C_B represents the cost of the bare module in dollars. The pressure factor, F_P, for each heat exchanger was determined by the following relation[16]:

$$F_P = 0.9803 + 0.018\left(\frac{P}{100}\right) + 0.0017(\frac{P}{100})^2$$
$$P \equiv tube\ side\ pressure\ (psia)$$

The materials factor, F_M, for the heat exchangers was determined by the following relation[17]:

$$F_M = a + (\frac{A}{100})^b$$

A represents the total area of the heat exchanger and a and b are coefficients based on the material of construction for the heat exchanger shell side and tube side respectively. Since all of the heat exchangers in our plant's heat exchanger network are constructed from carbon steel for both the shell-

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[15] Seider, 2004

[16] Seider, 2004

[17] Seider, 2004

side and tube-side, the coefficients a and b are both equal to 0. Therefore, F_M for all heat exchangers in our heat exchanger network is equal to 1.

The tube-length correction factor, F_L, was determined from the following table:

Tube Length (ft)	F_L
8	1.25
12	1.12
16	1.05
20	1

Table 22: Tube-length Correlation Factors

Source: UPENN, *Equipment Sizing and Capital Cost Estimation*

 The average tube-length for the heat exchangers is approximately 8 ft. therefore a correction factor of 1.25 was used for all of the heat exchangers.

The bare module cost, C_B, for a U-tube heat exchanger was calculated as follows[18]:

$$C_B = \exp\{ 11.147 - 0.9186[\ln(A)] + 0.09709[\ln(A)^2]\}$$

$$A \equiv total\ heat\ exchanger\ area\ (ft^2)$$

The following is a detailed sample calculation of how the purchase cost for HEX 1, which is the flue gas compressor after-cooler, was determined:

$$F_P = 0.9803 + 0.018\left(\frac{P}{100}\right) + 0.0017\left(\frac{P}{100}\right)^2$$

$$P = 255\ psia$$

$$F_P = 0.9803 + 0.018\left(\frac{255}{100}\right) + 0.0017(\frac{255}{100})^2 = 1.04$$

$$F_M = 1$$

$$F_L = 1.25$$

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[18] Seider, 2004

$$C_B = \exp\{11.147 - 0.9186[\ln(A)] + 0.09709[\ln(A)^2]\}$$

$$A = 561.9 \; ft^2$$

$$C_B = \exp\{11.147 - 0.9186[\ln(561.9)] + 0.09709[\ln(561.9)^2]\} = \$10,461.1$$

$$C_P = 1.04 \times 1 \times 1.25 \times \$10,461.1$$

$$C_{P \; (HEX \; 1)} = \$13,563.45$$

HEX	Area (m²)	Tube Side Pressure (atm)	Shell Side P (atm)	Material	Cost ($)
20	7.55	6	6	Carbon Steel	10,150

Table 23: Natural Gas Processing & Steam Reforming Section Heat Exchanger Costs

HEX	Area (m²)	Tube Side Pressure (atm)	Shell Side P (atm)	Material	Cost ($)
14	23.525	28	29	Carbon Steel	11,800
15	31.85	26	5	Carbon Steel	12,300
5	20.075	26	29	Carbon Steel	12,000
4	60.8	26	5	Carbon Steel	14,900

Table 24: Water Gas Shift Section Heat Exchanger Costs

HEX	Area (m²)	Tube Side Pressure (atm)	Shell Side P (atm)	Material	Cost ($)
1	52.2	16.35	16.35	Carbon Steel	14,000
7	27.875	15.642	1	Carbon Steel	11,500
AC1	562.782	16	1	Carbon Steel	11,500
17	100.475	16	1	Carbon Steel	17,500
18	64.675	16	1	Carbon Steel	14,600
19	56.25	28	1	Carbon Steel	14,600

Table 25: Flue Gas Treatment Section Heat Exchanger Costs

HEX	Area (m²)	Tube Side Pressure (atm)	Shell Side P (atm)	Material	Cost ($)
12	39.6	16	1	Carbon Steel	12,500
13	52.4	64	1	Carbon Steel	17,200

Table 26: Dry Ice Production Section Heat Exchanger Costs

HEX	Area (m^2)	Tube Side Pressure (atm)	Shell Side P (atm)	Material	Cost ($)
8	15.3	52	1	Carbon Steel	12,500
9	15.45	131.25	1	Carbon Steel	20,100
10	15.65	328.125	1	Carbon Steel	60,000
11	15.825	820.312	1	Carbon Steel	286,000

Table 27: Hydrogen Product Processing Section Heat Exchanger Costs

The tables above show the costs for all heat exchangers in this process by section. The costs listed are estimated values based on the calculated values; they are rounded up to account for inflation and slight design variations. The most expensive heat exchangers are those used as after coolers for the hydrogen product processing section due to the high pressures involved, which result in high amount of heat.

COMPRESSOR COSTS

Compressors were costs were determined using an online cost estimation source.[19] These costs were based on the work done by each of the compressors. To reduce the capital cost of compressors, the compression ratios were minimized. Lower compression ratios mean less work done by the compressor on the process stream, which also means lower pressure changes. Centrifugal compressors and oil-free screw compressors (OFS) were the most commonly used, but for high pressures as in the case of the final compression stage of hydrogen product processing section, reciprocating compressors were chosen. The costs estimates obtained were then adjusted using the 2010 to 2007 CEPCI ratio to account for inflation and market changes.

Compressor	Work (kW)	BHP (hp)	Compressor Type	Cost ($)
1	3.78	5.07	Centrifugal	$12,085
13	5.67	7.6	OFS	$12,271
9	2.98	3.99	OFS	$7,995

Table 28: Natural Gas Processing & Steam Reformation Section Compressor Costs

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[19] Matches <http://www.matche.com/EquipCost/Compressor.htm>

Compressor	Work (kW)	BHP (hp)	Compressor Type	Cost ($)
10	26.22	35.16	OFS	$62,285
11	29.02	38.92	OFS	$66,933
12	28.98	38.86	OFS	$66,933

Table 29: Flue Gas Treatment Section Compressor Costs

Compressor	Work (kW)	BHP (hp)	Compressor Type	Cost ($)
6	23.19	31.1	OFS	$57,079
7	23.78	31.9	Centrifugal	$52,989
8	11.32	15.18	OFS	$19,522

Table 30: Dry Ice Production Section Compressor Costs

Compressor	Work (kW)	BHP (hp)	Compressor Type	Cost ($)
2	9.38	12.58	Centrifugal	$25,100
3	9.68	12.98	Centrifugal	$25,844
4	10.32	13.84	Centrifugal	$27,331
5	12.03	16.13	Reciprocating	$29,934

Table 31: Hydrogen Product Processing Section Compressor Costs

The most expensive compressors were those with the highest work output. The reciprocating compressors, while capable of handling high pressures, were found to be cheaper because of the very small pressure drops and consequently small work outputs.

PUMP COSTS

Pump	Max. Pressure (atm)	Actual Work (kW)	Type	Cost ($)
1	29	0.2	Reciprocating	6,660
2	8.8	0.1	Reciprocating	6,660
3	16	0.1	Reciprocating	7,340
Total				**20,660**

Table 32: Pump Costs

Pump costs could not be directly calculated based on the work because of the low work values and volumes. All calculated costs were overestimates and as a result an alternate method of estimating costs was required. Pump costs were estimated using Matche.[20] In general, the pump costs were very small due to the small volumes of the process stream being pumped. In addition, the work required for each of the pumps was also very small. The pump costs are summarized above in Table 32.

<div align="center">

TANK COSTS

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Initial cost estimates based on CAPCOST[21] data and design relations yielded inaccurate costs. While generally accurate for average tanks and vessels, the vessels for this process are quite small. The original costs calculated were extremely large given the size of the tanks. As a result, the costs were determined using a ratio; the following relation was used to scale down prices of larger tanks.

$$C_1 = C_2 \left(\frac{V_2}{V_1}\right)^{0.7}$$

For a tank of volume 7.57 m^3 (2000 gallons), the cost was determined using the chemical engineering cost estimation resource Matches.[22]

$$C_1 = 46700 \left(\frac{0.0045}{7.57}\right)^{0.7}$$

$$C_1 = \$258$$

The cost of the dry ice flash was found to be approximately $258. The total cost of all 5 flash tanks was estimated to be $1800. The hydrogen storage tank costs were estimated using the same relation. The cost of one vessel was found to be $7165. Since 24 vessels are required the total cost will be approximately $172,000. The total cost of all flash tanks and storage vessels was found to be approximately $190,000.

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[20] Matche <http://www.matche.com/EquipCost/PumpCentr.htm>

[21] Turton et al., 2003

[22] Matche <http://www.matche.com/EquipCost/Tank.htm>

UTILITY COSTS

Costing of utilities required utility consumption values given by PRO/II based on the design of reactors, heat exchangers, pumps, and separation units.

In general, the following relationship can be used to determine the annual cost of utilities given the consumption on an hourly basis:

$$Cost = consumption\ (per\ unit\ time) \times unit\ cost$$

$$Cost\ per\ year = consumption\ (per\ hour) \times \frac{24\ hours}{day} \times \frac{365\ days}{year}$$

Water	kg/hr	m3/hr	gal/hr	$/1000 gal	$/hr	$/yr
Feed	344.092	0.345	91.173		0.0073	58.35
Cooling	3562.241	3.573	943.876		0.0755	604.08
NG Comp.	82.761	0.083	21.929	0.08	0.0018	14.03
H2 Comp.	609.741	0.612	161.561		0.0129	103.40
Flue Comp.	1946.546	1.952	515.770		0.0413	330.09
CO2 Comp.	923.194	0.926	244.616		0.0196	156.55
Total						**662.43**

Table 33: Water Costs

Table 33 shows the total water usage for each section or component with a water requirement. The unit cost of water (current sale price) is $0.08 per thousand gallons. The process has been designed minimized water usage and as a result, the cost of water per year is only approximately $663, which is a relatively low amount especially in comparison with natural gas costs show below in Table 34.

Natural Gas	scm/hr	1000 scf/hr	$/1000 scf	$/hr	$/yr
Feed	70.282	2.482		22.46197	179,696
Combustion	25.766	0.910	9.05	8.234755	65,878
Total (Without Treatment)					**245,573.78**
ZnO Bed					**7,483.71**
Total (With Treatment)					**253,057.50**

Table 34: Natural Gas Costs

A large contribution to overall costs is the natural gas feed. The market cost of natural gas is approximately $2 per thousand gallons. The large volume of natural gas required to meet the production requirement and the market demand of hydrogen results in an annual natural gas expenditure of approximately $54,270. Another cost that arises because of the use of natural gas feed is the cost of the pretreatment. The ZnO bed contributes greatly to the total cost both by design and because of the adsorbent requirement. Table 34 shows the breakdown of natural gas usage and costs.

Electricity	kW	$/kWh	$/hr	$/yr
NG Comp.	12.49		0.75	5,993.91
Water Pumps	0.27		0.02	130.95
H2 Comp.	41.46	0.06	2.49	19,902.45
Flue Comp.	84.89		5.09	40,746.33
MDEA HEX	0.10		0.01	48.00
CO2 Comp.	59.61		3.58	28,612.82
Total				95,434.46

Table 35: Electricity Costs

The MDEA heat exchanger is an air-cooled heat exchanger that is used to cool the regenerated MDEA. The process for the regeneration MDEA requires the heating of the agent to remove the adsorbed carbon dioxide. The heated MDEA is then cooled using an air-cooled heat exchanger; this heat-exchanger requires electricity consumption. The work outputs from PRO/II were compiled for pumps with head greater than 20 meters, compressors, and the MDEA heat exchanger. The work outputs (kW) were used to determine the required electricity. Table 35 shows the electricity consumption breakdown by component.

Variable Cost	Annual Cost ($/year)
Water	662.43
Natural Gas	52,270.45
Electricity	95,434.46
Total Variable Cost	150,367.34

Table 36: Total Utility Costs

By Section	$/yr	% of total
Main Process	60,467.69	40.2%
H2 Compression	20,005.84	13.3%
Flue & Dry Ice	69,893.80	46.5%

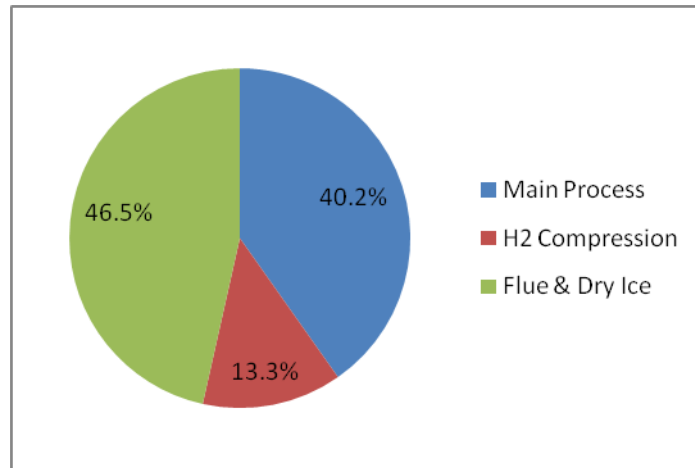*Table 37: Utility Cost Breakdown & Distribution*

Figure 15: Utility Cost Breakdown & Distribution

The breakdown of costs showed that the natural gas and electricity contribute the most to the total utility costs. To increase the cost efficiency of the plant, the electricity consumption must be reduced. Other options to reduce utility costs can be to use a pure methane feed. Pure methane feed usage will reduce losses because an extra reformer to break down higher hydrocarbons will not be required. In addition a pure methane feed is cheaper ($2/1000 scf as opposed to $9.05/1000 scf for natural gas), which would reduce feed costs. The largest utility costs come from the flue treatment and dry ice production sections. Carbon dioxide processing is the secondary purpose of this plant. This is a required section because of the no emissions policy of this project, which means that the utility costs of this section cannot be reduced since 100% of the carbon dioxide produced, must be converted and sold as dry ice. Table 37 and Table 38 show the utility cost breakdowns in detail; Figure 15 shows a pie chart with the percentage breakdown and distribution of utility costs by section.

Once all unit costs and utility costs were tallied, the overall cost analysis for the final plant design was completed. Building costs, labor costs, and rent were all included to determine total costs required for the plant per year. In addition, revenues and taxes were included and a complete cash flow analysis for the lifetime of the plant was performed.

CAPITAL COSTS

Capital Cost	$
Reactors	531,406
HEX	471,780
Compressors	466,300
Pumps	20,660
Flash Tanks	2,000
Storage Tanks	477,170
Plant Cost	2,089,155
Building Cost	522,289
Total	**2,611,444**

Table 38: Capital Cost Breakdown

The capital costs for the designed plant are summarized above in Table 38. The plant cost, which is the sum of all unit costs, totals to approximately $2.1 million. The building cost was approximated as follows:

$$\text{Building Cost} = 0.25 \times \text{Plant Cost}$$

The cost of building the plant was assumed to be approximately 25% of the total cost of the plant. For the current cost of the plant, the cost of building was found to be roughly $522,000. Although, exact values were not determined; this value was chosen as a reasonable estimate. The capital costs may vary significantly depending on the construction and building costs, which are heavily dependent on the location and the current market.

FIXED OPERATING COSTS

Fixed Cost	$/year
Catalyst	10,773
Adsorbent	82,472
Rent	480,000
Labor	648,000
MDEA	1160
Total	**742,405**

Table 39: Fixed Operating Cost Breakdown

Table 39 shows a summary of the fixed operating costs. Although these are yearly costs, it is important to note that the catalysts are replaced every 4 years while the adsorbents are replaced every five years. The largest cost contributions come from rent and labor. Possible solutions are obtaining government grants or subsidies to cover at least a portion of the rent costs. Rent and labor were found to be two of the three biggest cost sensitivities for this project.

VARIABLE OPERATING COSTS

Variable Cost	$/year
Water	663
Natural Gas	245,574
Natural Gas Treatment	7,484
Electricity	95,435
Total	**349,155**

Table 40: Variable Operating Costs Breakdown

Table 40 compiles the variable operating costs for the plant. The variable operating costs comprised of the annual utility costs and totaled to approximately $350,000 per year. The major sensitivity for the variable operating costs was found to be, as discussed, the natural gas feed cost.

Four different cases for the plant were developed to determine methods of maximizing profits during the 20 year lifetime of the plant. For each case, taxes, inflation, and revenues were included to determine the cumulative cash flow (CCF) during the 20 year span as well as discounted cash flow (DCF). The inflation rate was assumed to be approximately 3%. Taxes were taken on profits from the previous and were approximated to be 35% of those taxable profits. The discount rate was determined for each of the profitable cases, which were cases 2, 3, and 4. Figure 16, Figure 17, Figure 18, and Figure 13 show the cumulative cash flows and the discounted cash flows for each of the four cases studied.

Case 1: Original Project Specifications
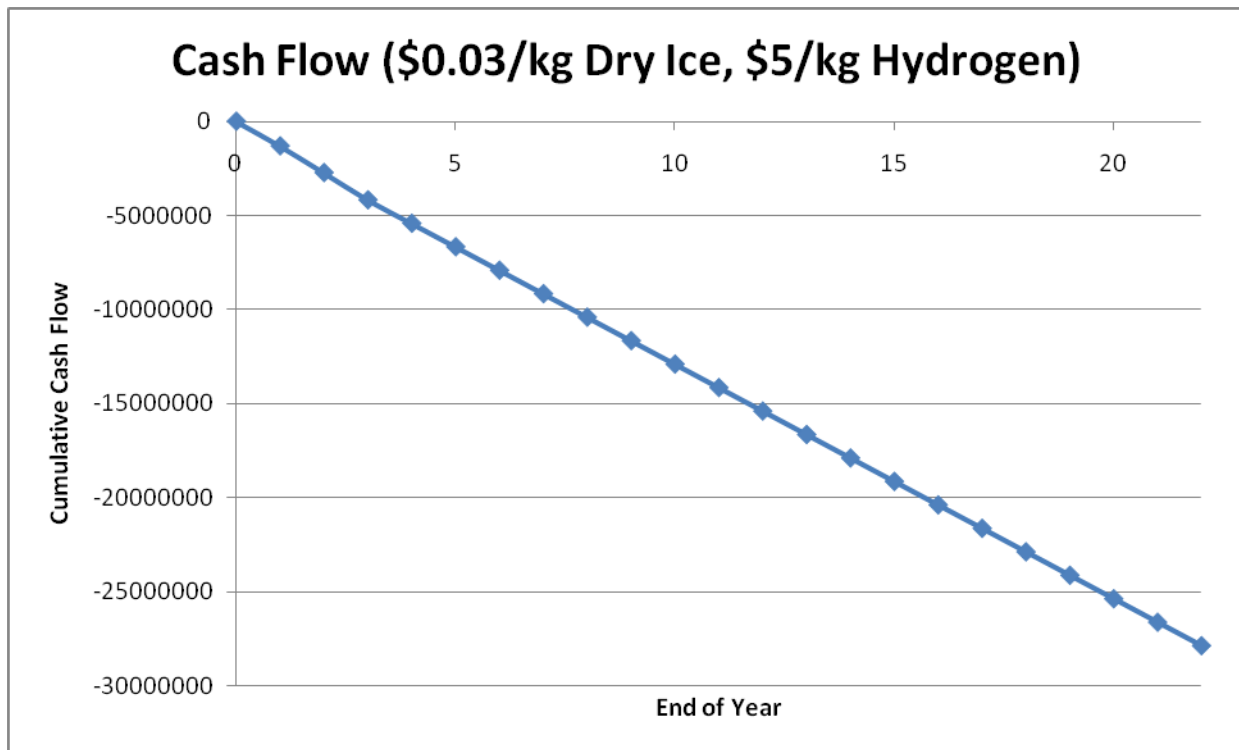
Figure 16: CCF Given Specifications

The original specifications of the project show no chance for profit as can be seen in Figure 16. At the end of the plant lifetime, the total loses total to approximately $28 million. There are three major costs that attribute to these losses: rent, labor, and product prices. However, since labor cuts directly affect production capacities as well as the safety of the plant, this was not changed. Rent and product prices were altered to determine how to best profit from the project.

Case 2: Increased Product Prices

Figure 17: Cash Flow (Adjusted Sales Prices)

Case 2 showed the most promise for this project. The current selling price of dry ice is $0.50 per kilogram as opposed to the original selling price of this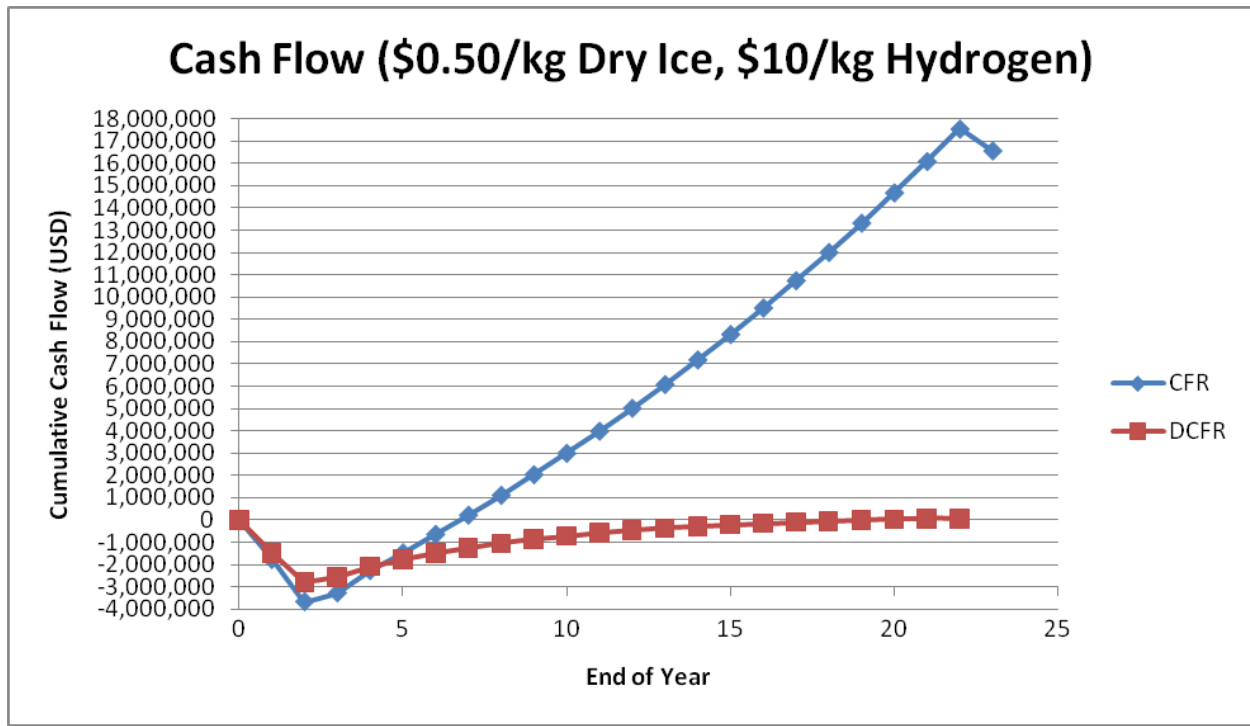 project, which was specified as $0.03 per kilogram. If the market price of dry ice is used and the price of the hydrogen product (originally $5.00 per kilogram) is doubled, the total cash flow during the last year of production reaches approximately $17.5 million. The breakeven point occurs during the middle of the fifth year. This breakeven point is slightly later than those of the following two cases. However, despite the later breakeven point, this case had the highest discount rate, which was found to be 20.12%, which means that the plant under these circumstances has the highest value by the end of its lifetime.

Cases 2 and 3 considered the possibility of subsidized rent along with an increase in one of the product prices. Case 2 doubled the hydrogen sale price while case 3 applied an increased dry ice sale price. Both showed a slightly earlier breakeven point. However, the discount rates were lower, which means that both cases 2 and 3 will have a lower present value at the end of the plant lifetime. Case 2 had a discount rate of 19.33% while case 3 had a slightly lower discount rate of 18.59%.

Case 3: Subsidized Rent & Increased Hydrogen Price
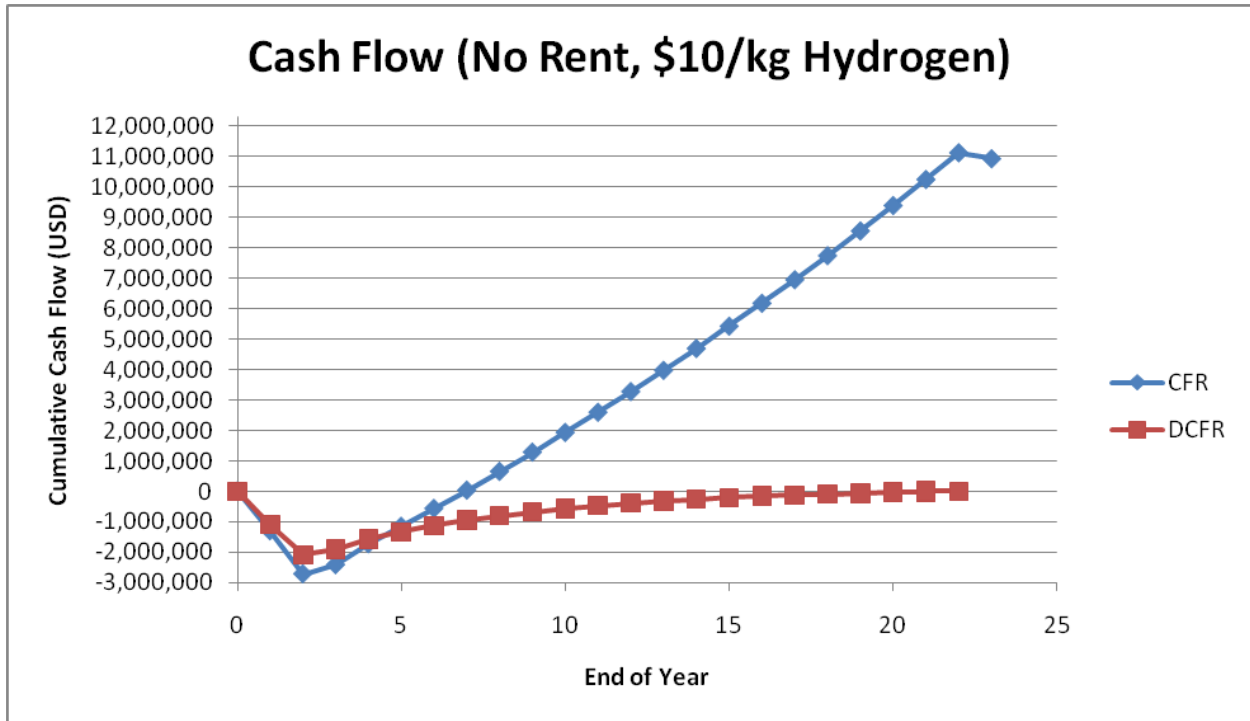
Figure 18: Cash Flow (No Rent, $10/kg Hydrogen)

Figure 18 shows the cumulative cash flow and discounted cash flow curves assuming rent is subsidized and the hydrogen sale price is doubled.

Case 4: Subsidized Rent & Increased Dry Ice Price
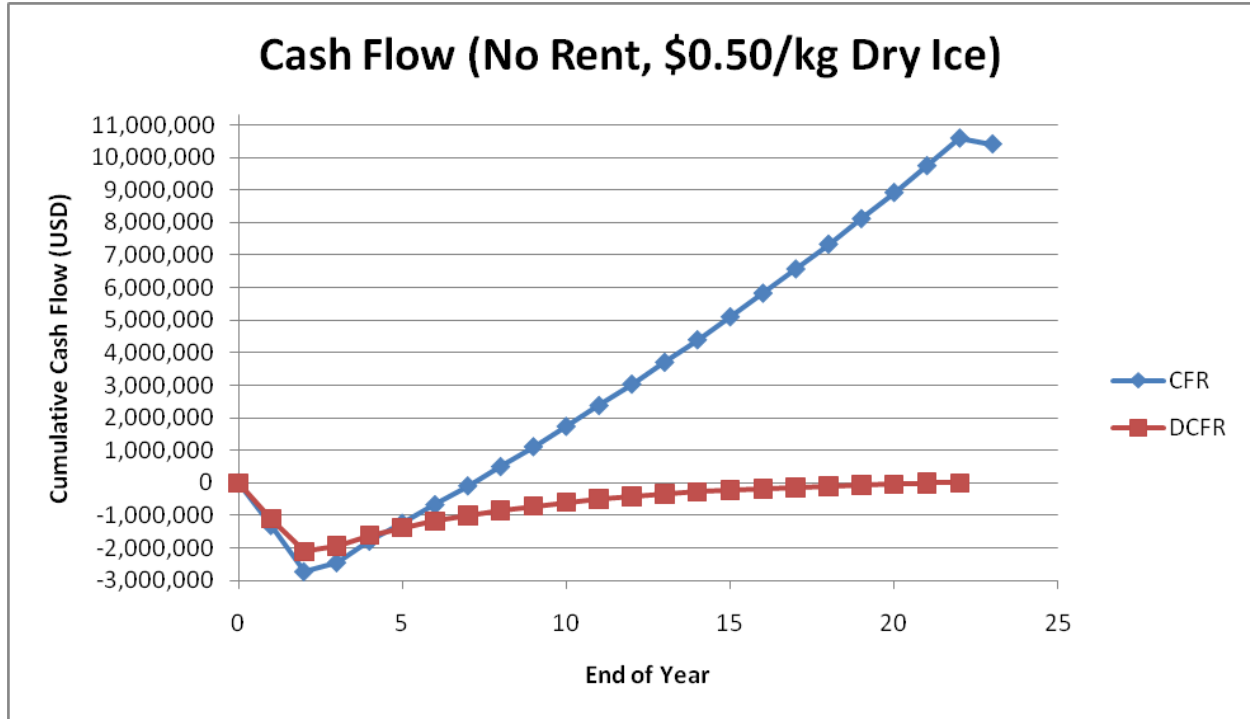
Figure 19: Cash Flow (No Rent, $0.50/kg Dry Ice)

Figure 19 shows the cumulative cash flow and discounted cash flow curves for case 4, which assumes subsidized rent and an increase in the dry ice sale price.

Ideally, the best case scenario would occur if rent were subsidized while product prices were increased to the specified values. However, from the three cases above, the best modification for the plant would be to increase sale prices, which ensures the highest profit and the highest discount rate.

PROCESS DESIGN

The main process objective of this project was to design a production plant that converted natural gas into H_2 product of 99.9999% purity. Our goal for H_2 production capacity was to produce enough H_2 to meet a fueling rate of 100 vehicles per day with a tank size specification of 4 kg at 700 atm. The goal for storage capacity was to store enough H_2 product for approximately 766 hours. Our success in achieving the desired purity of H_2 product was measured by analyzing the composition of the exit H_2 product stream from the final purification stage of the production process. Our success in achieving the production rate and storage capacity goals was measured by determining the amount of H_2 product yielded in our final plant design process and determining whether it satisfied both the production and storage capacity requirements.

Another process objective of this project was to design a H2 production process with high process efficiency. Our criteria for an efficient process were the following: an actual H2 yield close to the maximum theoretical yield, minimal utility consumption and energy input, and high recycle of waste product streams. Our success in achieving this objective was measured by comparing our plant to other H2 production plants and determining which plant satisfied our criteria the best.

ECONOMICS

The primary economic objective of this project was to design a plant that would earn profit before the midpoint of the lifetime of the plant. Our success in achieving this objective was measured by performing a complete cost analysis of the plant and determining the breakeven point for the plant's cumulative cash flow over its lifetime.

ENVIRONMENTAL & SAFETY FACTORS

The primary environmental objective of this project was to design a plant with zero carbon dioxide (CO_2), carbon monoxide (CO), and hydrogen sulfide (H_2S) emissions. Our plant is designed for zero CO2 emissions because CO2 is a heat-trapping greenhouse gas (GHG). Our plant is designed for zero CO and H2S emissions because CO and H_2S are classified by the EPA as toxic and hazardous wastes respectively. Our success in achieving the zero emissions objectives was measured by determining the amount of CO_2, CO, and H_2S yielded in our final plant design process.

The primary safety objective of this project was to design the physical layout of our plant in a way that minimized safety risks associated with our plant. Our success in achieving a plant design that had

minimal safety risks was measured by determining all of the safety risks posed by the plant and then determining how many safety risks were minimized as a result of the safety precautions that were implemented in our design.

OPERATORS

Unit	Number of Units	Worker per Unit	Workers per Shift	Total Number of Workers
Reactors/Separators	4	0.5	2	6
Pumps	3	0.2	1	3
Compressors	13	0.1	2	6
Heat Exchangers	21	0.1	3	9
Total				24

Table 41: Division of Labor

The data required for the division of labor and operator analysis was obtained from Turton et al.[23] The total number of operators required to run this plant is 24 per day. Table 41 shows the division of labor. This assumes 3 shift per day. In addition, due to the small sizes of the reactors and systems, reactors will be operated as systems. For example, the furnace and the steam reformers were considered one unit as were the high and low temperature shift reactors. The small size of the plant allows for individual worker to control multiple components that are in close proximity.

SUPERVISORS & CLERICAL ASSISTANCE

The required number of supervisors is directly related to the total number of workers during any one shift. The number of supervisors is also affected by the complexity of the processes. The unit operations are relatively simple for this plant, which will reduce number of supervisors required. Per shift, the plant requires 8 operators. For 8 operators, approximately 1 supervisor and 1 clerical assistant will be required for each shift, which means that in total there will be 3 supervisor postings for this plant and 3 clerical assistant positions.

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[23] Turton et al., 2003

Quality control is a very important aspect of this project because the cost per kilogram of hydrogen is very high, which means that the product must meet the market standards of this project. Hydrogen must be sampled regularly and analyzed to ensure that the purity is 99.9999%. The best method of testing the samples is by using gas chromatography mass spectrometry (GCMS). It is reccomended that the project investment includes the purchase of a GCMS. This is a valuable investment because samples must be taken from the process and analyzed three times a day. At the beginning of every shift, the operator in charge of the hydrogen storage tanks must sample the product and analyze it using the GCMS. The sampling and testing must occur three times a day because the plant only has an excess storage capacity of one day, which means that quality control must be accounted for at all times. Impure product would result in significant loss of revenue. Operators in charge of the hydrogen storage must be trained to take the appropriate sized samples and run the GCMS. GCMS outputs must also be accurately read in order to determine the quality and composition of product. All operators must be trained to use the GCMS in order to understand how individual unit operations affect the product and the sample readings. All operators must also be trained to make adjustments immediately as needed depending on the GCMS output.

Safety precautions were taken in the design of the plant to assure minimal risk to employees of our H_2 production plant. A major safety risk associated with our plant is the leakage of poisonous gases from process equipment due to failures in the equipment. The primary gases of concern are H_2S and CO.

H_2S is a flammable, toxic, and hazardous gas that has a strong characteristic odor of rotten eggs. The exposure pathways for H_2S are inhalation and dermal. If inhaled in high concentrations, H_2S can cause unconsciousness, coma, or even death. Dermal contact with H_2S can cause irritation to the skin in the form of frostbite. To prevent emissions of H_2S from the plant, excess ZnO adsorbent is used in the pre-treatment stage of the H_2 production process to assure complete removal of H_2S from the natural gas feedstock. The adsorbent must be replaced annually to maintain its complete loading performance. Since H_2S is classified by the US EPA as hazardous waste, the employees of the plant that work in the pre-treatment stage of the plant must have proper training in hazardous waste disposal and be educated on the regulations for hazardous waste handling established by the Resource and Recovery Act (RCRA). Employees will be required to wear protective eye wear, thermally insulated gloves, static resistant clothes, and safety shoes when handling containers of the H_2S. Detectors for H_2S are attached to process equipment in the pre-treatment stage. Automatic monitoring equipment for oxygen and the presence of potentially explosive air-gas mixtures is also installed in the pre-treatment stage and throughout the plant. Local exhaust ventilation has been implemented in the plant design to ensure that H2S does not exceed exposure limits to employees working in the plant.

In the case a leakage does occur, the employees will be trained on how to respond appropriately to the emergency with regards to who to call, fire fighting measures to be taken in the case of a fire, accidental release measures to be taken, and first aid measures in the case someone does get injured. Material Safety Data Sheets (MSDS) for hydrogen sulfide will be provided to all employees and will be located near process equipment in the pre-treatment stage. Fire extinguishers will also be located throughout the pre-treatment stage and the rest of the plant since our production plant deals with extremely flammable gases.

CO is a toxic, colorless, and odorless gas. The exposure pathways for CO are inhalation and dermal. If inhaled, CO exposure can cause target organ damage and even fatality if inhaled in high concentration. Dermal contact with CO can cause frostbite or burns to the skin. To prevent CO emissions from the plant, our plant has been designed to convert all intermediate CO into CO_2 and H_2 in the temperature shift reaction stages. CO that is not converted in this stage of the process is recovered in the PSA. The PSA adsorbent will be replaced every four years to maintain optimal performance and

complete loading of CO.   Employees that will dispose of the PSA adsorbent will be trained in proper handling methods of CO. All employees that will work in stages of the process where CO can be emitted will be required to wear properly fitted air-purifying or air-fed respirators, safety eyewear, chemically resistant and impervious gloves, and chemically resistant clothing. Local exhaust ventilation has been incorporated in the design of the plant and CO detectors are attached to the reformer, HTS, and LTS reactors as well as the PSA. The same emergency response measures and training will be taken in the case of a CO leakage as for a H_2S leakage.

Another major safety risk of our plant is the potential for explosions to occur due to the high temperature and high pressure operating conditions of the equipment and the high flammability of the gases that they contain. The reactors of the plant, especially the steam reformers, are operated at extremely high temperatures. Materials of construction for these high temperature reactors are thermally resistant and therefore will not melt under the reactor operating conditions. Temperature detectors are attached to all process equipment to monitor the internal temperatures of the equipment. Control engineers will be employed at our plant and will monitor the operating temperatures and pressures of all process equipment in the plant. They will be trained on how to respond if the temperatures or pressures exceed the maximum of the safe operating range for each type of equipment. Equipment that operates at high pressures will be double-contained to avoid material failure and consequently a possible explosion. Routine inspections of process equipment will be made by plant engineers in order to identify any failures in the equipment and take immediate action to fix any mechanical failures.

Since our plant deals with highly flammable gases, it is important to eliminate exposure of these gases to oxygen in the air. Therefore, most of the major equipment in our plant will be located underground to avoid risks of explosion.

ENVIRONMENTAL TARGETS

The environmental targets for our H_2 production plant are zero H_2S, CO, and CO_2 emissions and minimal wastewater production.

The processes involved in our H_2 production plant produce H_2S, CO, and CO_2. H_2S is a colorless gas characterized by its strong rotten egg odor and is classified by the US Environmental Protection Agency (EPA) as a hazardous waste. H_2S naturally occurs in the natural gas feedstock to our production plant. The total sulfide composition of the natural gas feedstock is approximately 0.2 mol%. The H_2S in the natural gas is removed by adsorption in the ZnO bed prior to the steam reformation stages. ZnO was chosen as the pre-treatment adsorbent because it can achieve almost complete loading of H_2S. In order to assure that our production plant has zero H_2S emissions, we have designed the ZnO bed to hold more adsorbent than is necessary to treat the amount of natural gas that will be processed in our plant. Excess adsorbent ensures complete removal of H_2S from the natural gas process stream in the pre-treatment stage and consequently yields zero emissions. To maintain complete loading of H_2S on the ZnO bed, the adsorbent is replaced on a yearly basis.

CO is a toxic gas that is produced in the steam reformation stage of the H_2 production process. CO is a pollutant that contributes to smog formation and the US EPA's maximum allowable level for CO in the air is 9 parts per million (ppm). CO is an intermediate product of the H_2 production process that is converted to CO_2 and H_2 in the temperature shift reaction stages. The CO product from steam reformation is reacted with steam in the temperature shift reactors at significantly lower temperatures than steam reformation. The temperature shift reactions favor low temperatures to achieve high conversion of CO. Therefore, to assure that all CO produced in our plant is converted to H_2 and CO_2, we use two temperature shift reactors that operate at different temperature ranges. The CO-rich product stream from the steam reformer is first processed in a high temperature shift (HTS) reactor and then is processed through a low temperature shift (LTS) reactor. Since the temperature shift reactions favor low temperatures for high conversion, the LTS reactor, which operates at a lower temperature range than the HTS, is used to convert any remaining CO that was not reacted in the HTS. CO that is not converted by the HTS and LTS is then captured in the pressure swing adsorber (PSA) to ensure that no CO emissions are made from the plant. To maintain complete loading of CO on the PSA adsorbent, the adsorbent will be replaced every 4 years.

CO_2 is a greenhouse gas that traps heat in the atmosphere and is known to contribute to global warming. In 2009, the US EPA officially declared CO_2 a dangerous air pollutant and established the

legislative framework for CO_2 regulations on emissions that will be enforced in the upcoming years under the Clean Air Act. CO_2 is produced in the temperature shift reaction stages of the H_2 production process, is separated and recovered from the H_2-rich process stream in the PSA, and is recycled for use as furnace combustion fuel as part of the PSA off-gas. CO_2 is a component in the flue gas exit stream of the furnace. The CO_2-rich exit flue gas is processed through the MDEA scrubber which removes 99.5% CO_2 from the flue gas. CO_2 is released from the CO_2-rich MDEA via heating and is converted into dry ice. Although the environmental target for the plant is zero CO_2 emissions, the MDEA scrubber doesn't recover all of the CO_2 from the flue gas. Therefore, the plant has emissions rate of 48,000 kg of CO_2 per year in the exit flue gas from the scrubber.

Our H_2 production plant generates 283,190 gallons of wastewater per year from condensation of the process stream. The wastewater is not contaminated with any hazardous or toxic chemicals therefore it does not need to be treated and does not pose any risks to environmental health.

SAFETY TARGETS

The safety targets for our plant are minimal risk for explosion, prevention of poisonous gas releases, and minimal safety risk to our workers and residents near the plant site.

H_2 is a highly combustible gas when it comes into contact with air therefore precautions were taken in designing the physical layout of the plant to ensure minimal risk of explosion. The majority of the equipment for the plant, specifically the compressors, heat exchangers, and hydrogen storage tanks are located underground. Therefore, if a H_2 leak were to occur, there will be less oxygen available underground to produce a large explosion and less damage to surrounding buildings would occur.

Much of the equipment in our H_2 production plant is operated at very high pressures and high temperatures therefore measures must be taken to prevent explosions that can be caused by equipment failure. High temperatures in reactors can be dangerous if they exceed the operating range limit. High temperatures can melt the reactor vessel material which can consequently result in the release of toxic materials from within the reactor. To avoid this problem, temperature monitors will be used to make sure that the operating temperatures of a reactor do not exceed the safe operating range. High operating pressures can also pose safety risks if they exceed the operating limit because they can cause equipment explosions. To avoid this, all high pressure equipment in our plant has a double layer of containment.

Our plant site is located in a densely populated residential area in New York City therefore appropriate measures were taken in the design of our plant and in the training of our employees to make sure that the residents of the surrounding community are not put at risk as a result of our plant

operations. Since our plant produces H_2S and CO, both of which are poisonous gases, we modified our design to achieve zero emissions of these gases. All of the H_2S from the process is captured by excess adsorbent in the pre-treatment stage therefore eliminating the risk of H_2S emissions. With regards to the CO, in the case that there is a leak in our plant equipment, we attached CO detectors to all of the process equipment. CO is a colorless and odorless gas therefore detectors must be used to determine if CO leakage has occurred. If the detectors indicate any level of CO, action will be taken to pinpoint the source of leakage and correct the failure in the equipment.

Proper training of our H_2 production plant employees is also essential in reducing safety risks of the plant. Control engineers will be employed in our plant to monitor the operating conditions of all the equipment and make sure that the equipment doesn't malfunction. Routine daily inspections will be made by plant operations employees to check for any damaged equipment or piping. Fueling station operators who fuel the vehicles will be trained in proper materials handling. Safety training will be provided to all our plant employees so that as little damage as possible is caused on the plant and the surrounding area in the case of an emergency situation.

SUPERVISOR GOALS

The supervisor is expected to ensure that all goals are met on time. There should be meetings with the design team weekly to ensure deadlines and goals are met. Once construction begins, weekly meetings should be scheduled to obtain information about progress and to ensure goals and deadlines are met. It is important to be aware of the design and constructions that come up. Necessary conferences and meetings should be scheduled to address problems, questions, and concerns. An open forum must be scheduled to allow the affected general public to ask questions and raise concerns about the project. The goal is to have the plant begin producing within 12 months of the first design meeting.

DESIGN TEAM GOALS

Weekly progress reports are required to ensure that all parties involved are updated on the design progress. Design team must initially have weekly meetings with the supervisor to go over design progress and discuss any design issues. Design of the plant should be completed within 3 months so that construction can begin. Once construction begins, the team must meet weekly with the construction team to ensure goals and deadlines are met. It is important that any design issues during construction are brought up and managed immediately to avoid delays in the project.

CONSTRUCTION TEAM GOALS

The construction team must begin work immediately after all designs are completed. It is required that the team meets with the design team weekly with progress reports. All construct and design issues must be brought immediately to both the design team as well as the supervisor to avoid delays. The construction of the plant must be completed within 8 months of the month that the design is completed. 1 month is then allowed for implementation, safety, and environmental checks. The operation of the plant must begin at the beginning of the following year.

PRODUCTION GOALS

The reactors and separators must be constructed by the end of the fourth month of construction. The remaining time will be allotted for the implementation of pumps, compressors, pipelines, storage tanks, flash tanks, and safety components. The plant, during the first year, will have a production rate of 75% capacity. By the second year, the plant must be operating at 100% capacity.

From our design and economic analysis of the NYC Hydrogen Fueling Station, we have determined that the plant is profitable for increased sale prices or reduced rent. However, the performance and profitability of the plant can be improved during operation with both process improvements and economic decisions.

Process improvements proposals should be developed during times of normal operation when there are no maintenance issues. Process engineers will meet once a week to discuss potential modifications or upgrades to the plant that can improve its performance. For example, a proposed modification may be to change the PSA adsorbent from pure zeolite 5A to a mixture of zeolite 5A and activated carbon. The discussion of this modification will evaluate the cost savings from changing the adsorbent and the impact it will have on the product quality, if any. If a process modification is agreed upon, a strategy for implementing the modification will be developed to minimize the plant shut-down time required. An important factor in evaluating a process improvement is the impact it may have on the hydrogen supply to the customers. In particular, if the improvement requires less than 24 hours of shutdown time, hydrogen should still be continuously available to the customers.

Ongoing market research should be performed by the marketing department to determine proper pricing of the products. The hydrogen sale price should be set competitively compared to the prices of nearby fueling stations. The plant is currently designed to produce a small surplus of hydrogen in addition to that being sold as on-site vehicle fuel. During periods of reduced customers (i.e. the winter season) it may be profitable to sell the surplus hydrogen to other markets, such as ammonia production. Finally, the hydrogen fuel economy is frequently subsidized by the government due to the push towards cleaner vehicle fuels. Thus, every effort should be made to apply for additional government subsidies during plant operation.

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```
% smr.m
% Models a the SMR reactor (conversion vs residence time)

% Operating conditions
T = 1123.15;   % Kelvin
P = 28;        % atm

% Constants
R = 8.314472;   % J/(K*kmol)

% Catalyst
kg_cat = 200;   % kg of catalyst to be used

% Feed parameters
n_total = 16.283;          % total feed, kmol/hr
x_feed = [0.176697323 0.75188684 0.04965029 0.018599342 0.001458712];   % feed composition
n_feed = n_total*x_feed;  % component molar rates, kmol/hr

% Calculate the volumetric flow rate (m^3/hr)
V = 1000*(n_total)*R*T/(101325*P);

% Time parameters
h = 0.000001;              % Step size (hours)
t = 0:h:0.00416666667;     % Time range

% Initialize mole array
n = zeros(length(t),5);
n(1,:) = n_feed;
% Initialize partial pressure array
p = zeros(length(t),5);
p(1,:) = P*x_feed;
% Initialize heat duty array
duty = zeros(size(t));

% Perform Runge-Kutta order 4 to caluclate molar amounts and heat duty
% with respect to residence time.
for i = 1:length(t)-1
    K1 = h*kg_cat*react(p(i,:),T);
    K2 = h*kg_cat*react(srk(n(i,:) + K1/2, V, T), T);
    K3 = h*kg_cat*react(srk(n(i,:) + K2/2, V, T), T);
    K4 = h*kg_cat*react(srk(n(i,:) + K3, V, T), T);
    n(i+1,:) = n(i,:) + (K1 + 2*K2 + 2*K3 + K4)/6;
    p(i+1,:) = srk(n(i+1,:), V, T);
    duty(i) = (n(i+1,:) - n(i,:))*[51638.7643 76678.6480 24813.5866 27960.2623 53621.7020]'/h;
end

%% Make plots
% Component molar flow rate as a function of residence time
figure(1);
plot(t*3600,n);
xlabel('Residence Time [s]');
ylabel('Moles/hour');

% Reactor duty per unit length along the reactor
figure(2);
plot(t*3600*3.2564,duty*h);
xlabel('Reactor Length [m]');
```

```
ylabel('Duty [kW/m]');

% Total duty with residence time
figure(3);
plot(t*3600,cumsum(duty*h));
xlabel('Residence Time [s]');
ylabel('Total Duty [kW]');
```

Listing 1: smr.m - A script used to produce a plot of component molar flow rate with respect to residence time.

```
function [ rate ] = r1( p_atm, T )
%R1 Rate equation for reaction 1
%   CH4 + H2O = CO + 3H2
%   p_atm = partial pressure array [CH4, H2O, H2, CO, CO2] in atm

R = 8.314472;        % Gas constant in J/kmol-K
p = 1.01325*p_atm;   % Converts pressure from atm to bar

k1 = 4.225e15*exp(-240100./(R*T));    % Rate constant
K1 = exp(-26830./T + 30.114);         % Equilibrium constant

kCO = 8.23e-5*exp(70650./(R*T));
kCH4 = 6.65e-4*exp(38280./(R*T));
kH2O = 1.77e5*exp(-88680./(R*T));
kH2 = 6.12e-9*exp(82900./(R*T));

Den = 1 + kCO.*p(:,4) + kH2.*p(:,3) + kCH4.*p(:,1) + kH2O.*p(:,2)./p(:,3);

rate = k1./Den.^2.*(p(:,1).*p(:,2)./p(:,3).^2.5 - p(:,3).^0.5.*p(:,4)./K1);

end
```

Listing 2: r1.m - Rate equation for steam reforming reaction (1).

```
function [ rate ] = r2( p_atm, T )
%R1 Rate equation for reaction 2
%   CO + H2O = CO2 + H2
%   p_atm = partial pressure array [CH4, H2O, H2, CO, CO2] in atm

R = 8.314472;
p = 1.01325*p_atm;   % Converts pressure from atm to bar

k2 = 1.955e6*exp(-67130./(R*T));    % Rate constant
K2 = exp(4400./T - 4.036);          % Equilibrium constant

kCO = 8.23e-5*exp(70650./(R*T));
kCH4 = 6.65e-4*exp(38280./(R*T));
kH2O = 1.77e5*exp(-88680./(R*T));
kH2 = 6.12e-9*exp(82900./(R*T));

Den = 1 + kCO.*p(:,4) + kH2.*p(:,3) + kCH4.*p(:,1) + kH2O.*p(:,2)./p(:,3);

rate = k2./Den.^2.*(p(:,4).*p(:,2)./p(:,3) - p(:,5)./K2);

end
```

Listing 3: r2.m - Rate equation for steam reforming reaction (2).

```
function [ rate ] = r3( p_atm, T )
%R1 Rate equation for reaction 3
```

```
%   CH4 + 2H2O = CO2 + 4H2
%   p_atm = partial pressure array [CH4, H2O, H2, CO, CO2] in atm

R = 8.314472;
p = 1.01325*p_atm;  % Converts pressure from atm to bar

k3 = 1.020e15*exp(-243900./(R*T));  % Rate constant
K1 = exp(-26830./T + 30.114);
K2 = exp(4400./T - 4.036);
K3 = K1.*K2;                        % Equilibrium constant

kCO = 8.23e-5*exp(70650./(R*T));
kCH4 = 6.65e-4*exp(38280./(R*T));
kH2O = 1.77e5*exp(-88680./(R*T));
kH2 = 6.12e-9*exp(82900./(R*T));

Den = 1 + kCO.*p(:,4) + kH2.*p(:,3) + kCH4.*p(:,1) + kH2O.*p(:,2)./p(:,3);

rate = k3./Den.^2.*(p(:,1).*p(:,2).^2./p(:,3).^3.5 - p(:,3).^0.5.*p(:,5)./K3);

end
```

Listing 4: r3.m - Rate equation for steam reforming reaction (3).

```
function [ p ] = srk( n, V, T )
%SRK Soave-Redlich-Kwong equation of state.
%   n is in kmol, V is in m^3, T is in K, and p is in atm.
%   Component order: [CH4, H2O, H2, CO, CO2]

Tc = [190.564 647.096 33.19 132.92 304.21];        % Critical temperatures
Pc = [4.599e6 22.064e6 1.313e6 3.499e6 7.383e6];   % Critical pressures
omega = [0.0115 0.3449 -0.216 0.0482 0.2236];      % Acentricity factors
R = 8.314472;  % Gas constant, J/kmol-K

Tr = T./Tc;    % Calculate reduced pressure

% Calculate constants
alpha = (1 + (0.48508 + 1.55171*omega - 0.17613*omega.^2).*(1 - Tr.^0.5)).^2;
alpha(1) = 1.202*exp(-0.30288*Tr(1));
a = 0.42748*R^2*Tc.^2./Pc;
b = 0.08664*R*Tc./Pc;

% Calculate pressure (atm)
p = (R*T./(V./(1000*n) - b) - a.*alpha./(V./(1000*n).*(V./(1000*n) + b)))/101325;

end
```

Listing 5: srk.m - Implentation of Soave-Redlich-Kwong equation of state.

```
function [ n_rate ] = react( p_atm, T )
%REACT Combines rate equations as a single reaction function.
%       p_atm = partial pressure array in atm [CH4, H2O, H2, CO, CO2]
%       T =     Temperature in Kelvin

r_1 = r1(p_atm, T)';
r_2 = r2(p_atm, T)';
r_3 = r3(p_atm, T)';

n_rate = [-(r_1 + r_3), -(r_1 + r_2 + 2*r_3), 3*r_1 + r_2 + 4*r_3, r_1 - r_2, r_2 + r_3];
```

```
end
```

Listing 6: react.m - Combines reaction rates to calculate differential change in molar amount for each component.


```
% Models the HT-WGS reactor (conversion vs residence time)

% Operating conditions
T = 623.15;   % Kelvin
P = 26.9714;  % atm

% Constants
R = 8.314472;    % J/(K*kmol)
kg_cat = 300;    % kg of catalyst to be used

% Feed info
n_total = 20.76761001;   % total feed, kmol/hr
x_feed = [0.030585237 0.424350506 0.420035252 0.065329892 0.058360273]; % feed composition
n_feed = n_total*x_feed; % component molar rates, kmol/hr

% Calculate the volumetric flow rate (m^3/hr)
V = 1000*(n_total)*R*T/(101325*P);

% Time parameters
h = 0.000001;                    % Step size (hours)
t = 0:h:0.00416666667;           % Time range

% Initialize mole array
n = zeros(length(t),5);
n(1,:) = n_feed;
% Initialize partial pressure array
p = zeros(length(t),5);
p(1,:) = P*x_feed;

% Perform Runge-Kutta order 4 to caluclate molar amounts
% with respect to residence time.
for i = 1:length(t)-1
    K1 = h*kg_cat*react_hts(p(i,:),T);
    K2 = h*kg_cat*react_hts(srk(n(i,:) + K1/2, V, T), T);
    K3 = h*kg_cat*react_hts(srk(n(i,:) + K2/2, V, T), T);
    K4 = h*kg_cat*react_hts(srk(n(i,:) + K3, V, T), T);
    n(i+1,:) = n(i,:) + (K1 + 2*K2 + 2*K3 + K4)/6;
    p(i+1,:) = srk(n(i+1,:), V, T);
end
```

Listing 7: hts.m - A script used to produce a plot of component molar flow rate with respect to residence time for the high temperature shift reactor.


```
function [ rate ] = r2_hts( p_atm, T )
%R1 Rate equation for reaction 2
%    CO + H2O = CO2 + H2
%       p_atm = partial pressure array [CH4, H2O, H2, CO, CO2] in atm

R = 8.314472;               % Ideal gas constant
p = 1.01325*p_atm;          % Converts pressure from atm to bar
c = p./(R*T);

K2 = exp(4400./T - 4.036);  % Equilibrium constant

Beta = c(5).*c(3)./c(4)./c(2)./K2;
rate = 3600*exp(26.1)*exp(-95000./(R*T)).*c(4).*c(2).*(1 - Beta);
```

```
end
```

Listing 8: r2_hts.m - Rate equation for steam reforming reaction (2) for the HTS reactor.

```
function [ n_rate ] = react_hts( p_atm, T )
%REACT Combines rate equations as a single reaction function.
%       p_atm = partial pressure array in atm [CH4, H2O, H2, CO, CO2]
%       T =      Temperature in Kelvin

r_1 = 0;
r_2 = r2_hts(p_atm, T)';
r_3 = 0;

n_rate = [-(r_1 + r_3), -(r_1 + r_2 + 2*r_3), 3*r_1 + r_2 + 4*r_3, r_1 - r_2, r_2 + r_3];

end
```

Listing 9: react_hts.m - Combines reaction rates to calculate differential change in molar amount for each component. (Modifed from react.m for the HTS reactor.)

```
% Models the LT-WGS reactor (conversion vs residence time)

% Operating conditions
T = 470;       % Kelvin
P = 26.96;     % atm

% Constants
R = 8.314472;   % J/(K*kmol)
kg_cat = 1000;   % kg of catalyst to be used

% Feed info
n_total = 20.76761001;   % total feed, kmol/hr
x_feed = [0.030585237 0.366471528   0.47791423    0.007450913   0.116239251]; % feed
composition
n_feed = n_total*x_feed; % component molar rates, kmol/hr

% Calculate the volumetric flow rate (m^3/hr)
V = 1000*(n_total)*R*T/(101325*P);

% Time parameters
h = 0.000001;                  % Step size (hours)
t = 0:h:0.00416666667;         % Time range

% Initialize mole array
n = zeros(length(t),5);
n(1,:) = n_feed;
% Initialize partial pressure array
p = zeros(length(t),5);
p(1,:) = P*x_feed;

% Perform Runge-Kutta order 4 to caluclate molar amounts
% with respect to residence time.
for i = 1:length(t)-1
    K1 = h*kg_cat*react_lts(p(i,:),T);
    K2 = h*kg_cat*react_lts(srk(n(i,:) + K1/2, V, T), T);
    K3 = h*kg_cat*react_lts(srk(n(i,:) + K2/2, V, T), T);
    K4 = h*kg_cat*react_lts(srk(n(i,:) + K3, V, T), T);
    n(i+1,:) = n(i,:) + (K1 + 2*K2 + 2*K3 + K4)/6;
    p(i+1,:) = srk(n(i+1,:), V, T);
```

```
end

%% Make plot
figure(1);
plot(t*3600,n);
xlabel('Residence Time [s]');
ylabel('Moles/hour');
```

Listing 10: lts.m - A script used to produce a plot of component molar flow rate with respect to residence time for the high temperature shift reactor.

```
function [ rate ] = r2_lts( p_atm, T )
%R1 Rate equation for reaction 2
%    CO + H2O = CO2 + H2
%       p_atm = partial pressure array [CH4, H2O, H2, CO, CO2] in atm

p = 1.01325*p_atm;  % Converts pressure from atm to bar
y = p./sum(p)*0.998661159;

rho_b = 90; % lb/ft^3
psi = 4.33;
K_eq = exp(-4.72 + 8640./(1.8*T));          % Equilibrium constant

rate = psi*exp(12.88 - 3340/1.8./T).*(y(4)*y(2) - y(5)*y(3)./K_eq)/(379*rho_b);

end
```

Listing 11: r2_lts.m - Rate equation for steam reforming reaction (2) for the LTS reactor.

```
function [ n_rate ] = react_lts( p_atm, T )
%REACT Combines rate equations as a single reaction function.
%       p_atm = partial pressure array in atm [CH4, H2O, H2, CO, CO2]
%       T =     Temperature in Kelvin

r_1 = 0;
r_2 = r2_lts(p_atm, T)';
r_3 = 0;

n_rate = [-(r_1 + r_3), -(r_1 + r_2 + 2*r_3), 3*r_1 + r_2 + 4*r_3, r_1 - r_2, r_2 + r_3];

end
```

Listing 12: react_lts.m - Combines reaction rates to calculate differential change in molar amount for each component. (Modifed from react.m for the LTS reactor.)

```
T = 311;            % Temperature in Kelvin
P = 16*101.325;     % Pressure in kPa

A = 32.45; B = -7440; C = 33; D = -18.5; % Constants
X_amine = .5;       % Mole fraction of amine in the clean solution

L = 0:0.0001:1;    % Loading (mol CO2 per mol amine)

% The equilibrium equation
K = exp(A + B./T + C*L.*X_amine + D*(L.*X_amine).^0.5);

% Construct equilibrium curve
X = L.*X_amine;
x = X./(1 + X);
Y = K.*x./(P - K.*x);
```

```
y = Y./(1 + Y);

% Define inlet and outlet conditions
x_in = 3.4903e-004; % Determined by regen.m
y_out = 0.005;
L_prime = 21;
V_prime = 27.10209839;

% Construct operating line
X_in = x_in./(1-x_in);
Y_out = y_out./(1-y_out);
Y_op = X.*(L_prime/V_prime) + Y_out - X_in*(L_prime/V_prime);

% Plot curves
figure(1)
plot(X,Y,X,Y_op);
[~, max_index] = min(abs(y - 1));
axis([0 0.22 0 0.16]);
xlabel('Moles of CO_2/mole of MDEA solution, X');
ylabel('Moles of CO_2/mole of CO_2-free gas, Y');
```

Listing 13: absorber.m - Script used to plot equilibrium line and operating line of MDEA absorber.

```
T_regen = 443.15;     % The regeneration temperature
P = 16*101.325;       % Pressure in kPa

A = 32.45; B = -7440; C = 33; D = -18.5;  % Constants
X_amine = 0.5;    % Mole fraction of amine in the clean solution

L = 0:0.001:1;    % Loading (mol CO2 per mol amine)

% The equilibrium equation
K = @(x) exp(A + B./T_regen + C*x./(1 - x) + D*(x./(1 - x)).^0.5);

% The function to solve
strip_eq =  @(x) exp(A + B./T_regen + C*x./(1 - x) + D*(x./(1 - x)).^0.5).*x./P - 1;

% Equilibrium CO2 in the regenerated MDEA solution
x_regen = fzero(strip_eq, 0.001)
```

Listing 14: regen.m - Script to determine the equilibrium concentration of dissolved carbon dioxide for a given temperature and pressure.