

## Sustainable Hydrogen Production by Steam-Methane Reforming: Plant Design and Economic Analysis

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### Executive Summary

This report seeks to evaluate the economic potential of hydrogen gas as a CO<sub>2</sub> free, sustainable fuel source for hydrogen fuel cell electric vehicles (HFCEVs). We propose a novel design for a chemical plant capable of producing 63 kilotons annually (KTA) of hydrogen gas, with a composition of 0.99999 wt % H<sub>2</sub> at a pressure of 30 bar, to be sold for \$1,300 per metric ton (MT). High purity hydrogen gas is traditionally made using a steam-methane reformer (SMR) followed by a water gas shift (WGS) reactor. Our design incorporates these reactions, but it is unique because all CO<sub>2</sub> produced is isolated and sequestered using an amine scrubbing system in order to eliminate all greenhouse gas emissions. The first two reactions are performed in two packed bed reactors (PBRs) that are placed in series. According to the reaction kinetics and various economic evaluations, the optimal reaction conditions were determined to be 880 °C and 20 bar for the SMR, and 300 °C and 20 bar for the WGS. These conditions maximize profit while still producing the specified amount of hydrogen gas. Optimal heat integration can be achieved by purchasing pure water at STP for \$0.05 per MT and pumping it through a network of 20 heat exchangers in order to heat it up before finally mixing it with the natural gas feed. The natural gas feed is purchased for \$132 per MT and is composed of 98 wt% CH<sub>4</sub> and 2 wt% CO<sub>2</sub>. The gas mixture is heated in a furnace and enters the first reactor at 880 °C and 20 bar. Natural gas is fed at a rate of 168 million (MM) kg per year, and water is fed at a rate of 476 MM kg per year corresponding to a feed molar ratio (MR) of 2.5:1. Assuming a 2-year construction period, we estimate that a total capital investment (TCI) of \$70 million would be required and can be financed with a 10-year bond at a fixed rate of 4%. After 12 years of operation the plant is projected to have an NPV of \$10.8 MM and an NPV% of 1.11%. The resultant economics are profitable, but do not fall in the acceptable range for a chemical plant. However, due to the environmental advantages of a CO<sub>2</sub>-neutral fuel source, it is likely that people would be willing to pay more in the future for fuel if it is clean. Further calculations found that if the sale price of the hydrogen product increases by 28.0% to \$1,670 per MT, the proposed plant would yield a positive NPV% of 10.0% per year after 12 years of operation. Under these assumptions, this design appears promising and would merit further investigation.

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## 1. Introduction

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One of the largest sources of carbon dioxide (CO<sub>2</sub>) emissions is gasoline-fueled vehicles. The issue of climate change has sprouted a clean-energy movement and has compelled Snell Oil Company, along with major automobile companies, to begin testing hydrogen-fueled electric vehicles. Unlike traditional fossil fuels, the combustion of hydrogen only produces steam as a byproduct. Moreover, hydrogen has a large energy density of 120 MJ/kg which is more than twice that of gasoline and more than 100 times greater than that of lithium batteries. To produce the necessary amount of hydrogen, Snell has developed two proprietary catalysts to facilitate steam reformation of methane.

### 1.1 Reaction Chemistry

Steam methane reforming involves a series of two independent gas-phase reactions (Rxn 1 and 2) and the overall reaction (Rxn 3).



Steam reforms methane in the endothermic first reaction to produce carbon monoxide (CO). The second reaction, which is an exothermic water-gas shift reaction, will produce CO<sub>2</sub> as a byproduct. A magnesium supported nickel catalyst (Ni-Mg) will facilitate all three reactions and their rate laws are modeled kinetically as surface adsorption reactions, where solid-gas interactions of each component are factored into the rate law. A copper/zinc oxide mixture supported on aluminum oxide (CZA) will exclusively catalyze the second reaction, which will now run according to a simple power-law kinetic rate law. Equations 1-5 represent the rate laws for our reactions, where  $r_4$  represents the CZA catalyzed reaction and  $p_i$  is each component's partial pressure. The values of the rate and equilibrium constants as a function of temperature can be found in Appendix B.

$$r_1 = \frac{1}{(p_{H_2} + \epsilon)^{2.5} \psi^2} (k_1 p_{CH_4} p_{H_2O} - k_{-1} p_{H_2}^3 p_{CO}) \quad (1)$$

$$r_2 = \frac{1}{(p_{H_2} + \epsilon) \psi^2} (k_2 p_{CO} p_{H_2O} - k_{-2} p_{H_2} p_{CO_2}) \quad (2)$$

$$r_3 = \frac{1}{(p_{H_2} + \epsilon)^{3.5} \psi^2} (k_3 p_{CH_4} p_{H_2O}^2 - k_{-3} p_{H_2}^4 p_{CO}) \quad (3)$$

$$r_4 = k_4 p_{CO} p_{H_2O} - k_{-4} p_{H_2} p_{CO_2} \quad (4)$$

$$\psi = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2} + \epsilon} \quad (5)$$

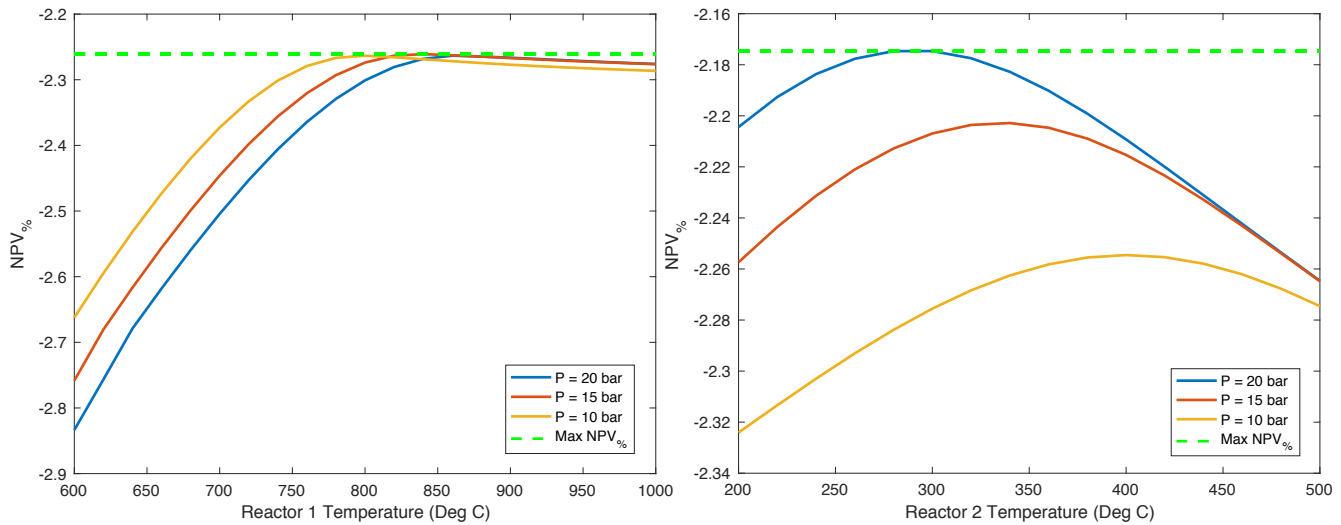
To favor the forward reactions, required conditions include a temperature range of 600-1000°C for Rxn 1-3 and 200-500°C for Rxn 4. The pressure must be within the range of 5-70 bar.

## 2. Plant Design/HYSYS Simulation

### 2.1 Conceptual Design and Optimization

The design process begins by modeling the production of hydrogen and determining optimal conditions for the reactors based on the desired outputs of the system. The reactions in each PBR were modeled in MATLAB by using the finite difference approximation to solve differential equations based on the reaction kinetics and mole balances on each species. Several variables were used to approximate energy input, equipment size, and operation cost. These approximations were then used to determine profitability and production rate. The main variables we tested are: temperatures in PBR 1 and 2 ( $T_1$ ,  $T_2$ ), pressure in the reactors ( $P$ ), conversion of limiting reactant ( $X_{CH_4}$ ,  $X_{CO}$ ), and the molar feed ratio of water to methane ( $MR$ ). Note that equipment costing was performed with Douglas's factored estimates [1], and NPV analysis results are from using Duncan Mellichamp's linear variable method [2].

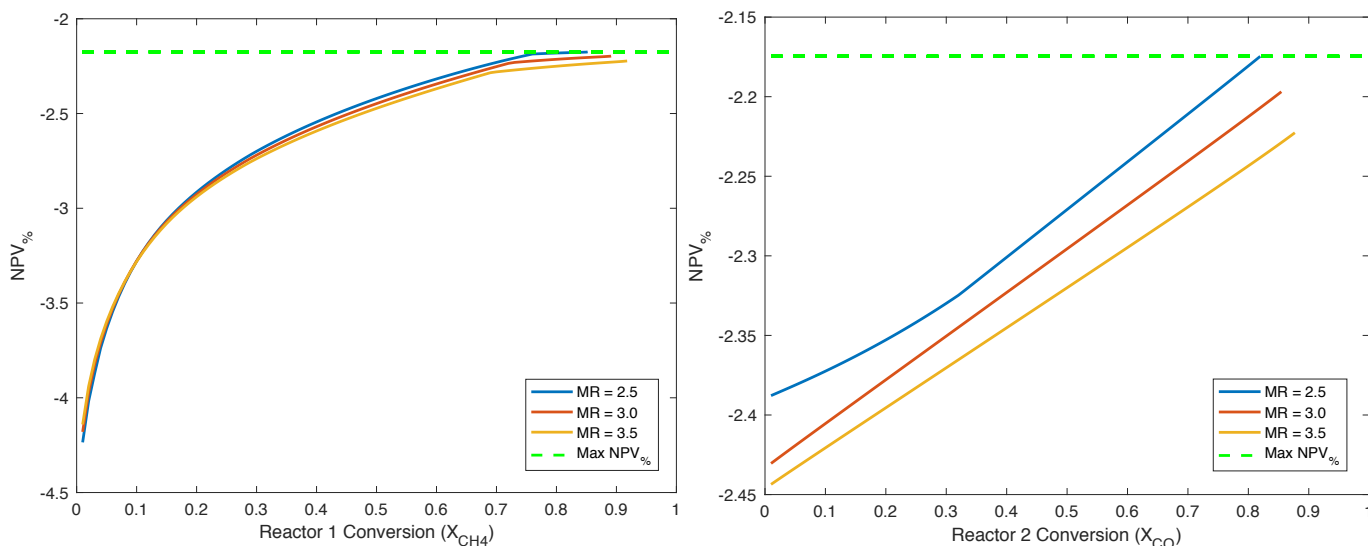
The first graphs are used to optimize the temperatures in PBR 1 and 2 ( $T_1$ ,  $T_2$ ) and the pressure of gases flowing through the reactors ( $P$ ) with the goal of maximizing NPV%. Fig. 1 plots NPV% against reactor temperature for both PBR 1 and 2 at varying system pressure.



**Figure 1.** Optimization plots for process variables  $T_1$  and  $P$  (left) and  $T_2$  and  $P$  (right). The optimal temperature and pressure settings are selected to maximize NPV% of the plant.

From the plots above, the optimal conditions are as follows: reactor 1 temperature is 880 °C, reactor 2 temperature is 300 °C, and the system pressure is 20 bar. The plot for reactor 2 has a peak in NPV% at  $P = 20$  bar and  $T_2 = 300$  °C, which makes sense because the reaction is exothermic, where equilibrium is shifted toward the products at lower temperatures. However, if temperature is too low, then the reaction will not be kinetically favorable and will proceed too slowly, so 300 °C is a reasonable choice that lies between the two extremes. For reactor 1, the maximum NPV% is achieved at 20 bar and 880 °C. The reactions in reactor 1 are endothermic, so higher temperatures cause a favorable shift in equilibrium. The chosen values of  $T_1$ ,  $T_2$ , and  $P$  will be fixed in subsequent optimization plots.

The remaining variables to be optimized are molar ratio of feed ( $MR$ ) and conversion of limiting reactant in reactors 1 and 2 ( $X_{CH_4}$ ,  $X_{CO}$ ). These variables are varied and are plotted with the resulting NPV% values in Fig. 2.



**Figure 2.** NPV% as a function of reactor conversions at molar ratios ( $MR$ ) of 2.5, 3.0, and 3.5. These plots are used to determine the optimal reactor conversions and molar ratio of the design.

From the above plot, we can determine that NPV% curves have the highest values when  $MR$  is set to 2.5 moles of water feed per 1 mole of methane feed. The maximum NPV% values of each plot correspond to a methane conversion ( $X_{CH_4}$ ) of 0.85 in PBR 1 and a carbon monoxide conversion ( $X_{CO}$ ) of 0.82 in reactor 2. The optimal conceptual design variables are as follows:  $X_{CH_4}$  is set to 0.85,  $X_{CO}$  is 0.82,  $T_1$  equals 880 °C,  $T_2$  equals 300 °C,  $P$  is set to 20 bar, and  $MR$  will be 2.5. The selected variables will now be applied to a HYSYS simulation of the plant to predict the feasibility of our design.

## 2.2 Separation Systems

The separation system includes one flash drum, a pressure swing adsorber (PSA), and an amine scrubber. After water is flashed out, the gas stream is condensed and sent into a PSA. The PSA system consists of four isothermal packed vessels operating in conjunction at 30°C. Zeolite 5A was used as the sorbent and adsorption data were obtained from literature [3]. Total mass of adsorbent was calculated by assuming 90% recovery of  $H_2$ , a five-minute adsorption time, and 95% load fraction. This mass was then used to determine an individual PSA volume of 32 m<sup>3</sup> while installation cost was determined using Douglas' factored estimates. Purified hydrogen leaves the PSA from one stream while a second exit stream of  $CO_2$ ,  $CO$ ,  $CH_4$ , and trace  $H_2$  is fed into the amine scrubbing system [4].

The amine scrubbing system consists of a carbon steel absorption column followed by a carbon steel distillation column with a reboiler. First, low pressure  $CO_2$  at 2 bar and 40°C is absorbed by a countercurrent liquid amine stream. Then, the liquid amine is purified by the 120°C stripping column and exits out the bottom. Purified gaseous  $CO_2$  exits from the top where it is sent to permanent storage by mineral sequestration [5].

## 2.3 HYSYS Simulation

The base-case conceptual design was implemented into Aspen HYSYS to simulate the operation of the plant. The previously optimized parameters, such as the reactor temperatures ( $T_1$ ,  $T_2$ ), pressure ( $P$ ), volumes ( $V_1$ ,  $V_2$ ), conversions ( $X_{CH_4}$ ,  $X_{CO}$ ), and feed molar ratio ( $MR$ ) were inserted directly into HYSYS. Subsequently, the feed rates and outlet flow rates were all inputted directly from the optimal conceptual design. After the conceptual design was successfully simulated, certain design choices, such as heat exchanger placement and coolant flowrates, were adjusted to maximize revenue and lower cost. These new parameter values were chosen for the base-case HYSYS design and for the final economic analysis. A comparison between the HYSYS and conceptual design can be found in Appendix B.

The Peng-Robinson fluid package was chosen, and the reactions were set up as heterogeneous catalytic reactions with the corresponding derived kinetic parameters (App. B). HYSYS simulated a full conversion of methane in the first reactor but extremely low conversion of CO in the second reactor even after varying temperatures and pressures. The pre-exponential factor for Rxn 4 was adjusted by a factor of 100 to better model the kinetics to account for solid-gas interactions.

The packed bed reactors were modeled as a plug-flow reactor with a catalytic bed. Our conceptual reactor sizing parameters were successfully simulated in HYSYS and reached the same conversion values as the MATLAB code. Reactor volumes of 93.6 m<sup>3</sup> and 104.8 m<sup>3</sup> were determined to be the optimal volumes for PBR 1 and PBR 2, respectively. These volumes correspond to the optimal conversions of methane (0.86) and carbon monoxide (0.82) determined in the conceptual design.

Heat exchangers were assumed to have a shell and tube design and no pressure drop. The maximum temperature difference between counter-current streams is 120°C, so a series of heat exchangers were necessary to gradually cool streams within this limit across a large temperature drop. Outlet feed temperatures were manually iterated and chosen to satisfy both the maximum temperature change and to avoid a temperature cross or fraction conversion error within the heat exchanger. Outlet feed temperatures were manually iterated and chosen to satisfy the maximum temperature change and to avoid a temperature cross or fraction conversion error within the heat exchanger. Similarly, the cooling water and cooling steam flow rates were also adjusted to provide enough coolant without causing too large of a temperature drop.

Other decisions made in HYSYS was pressurizing liquid water with a pump rather than feeding steam through a compressor. This was chosen for several reasons. The operational cost of a pump is significantly less than a compressor to pressurize the feed to 20 bar. Process water is \$0.05/MT at standard conditions while steam would have costed more than \$5/MT. It also functions as a coolant for half of the heat exchangers. It was decided to use both cooling water and steam because the water would stay in vapor liquid equilibrium between heat exchangers and prevent temperature change until it fully vaporizes into steam.

## 2.4 Process Flow Diagram of Base-Case HYSYS Design

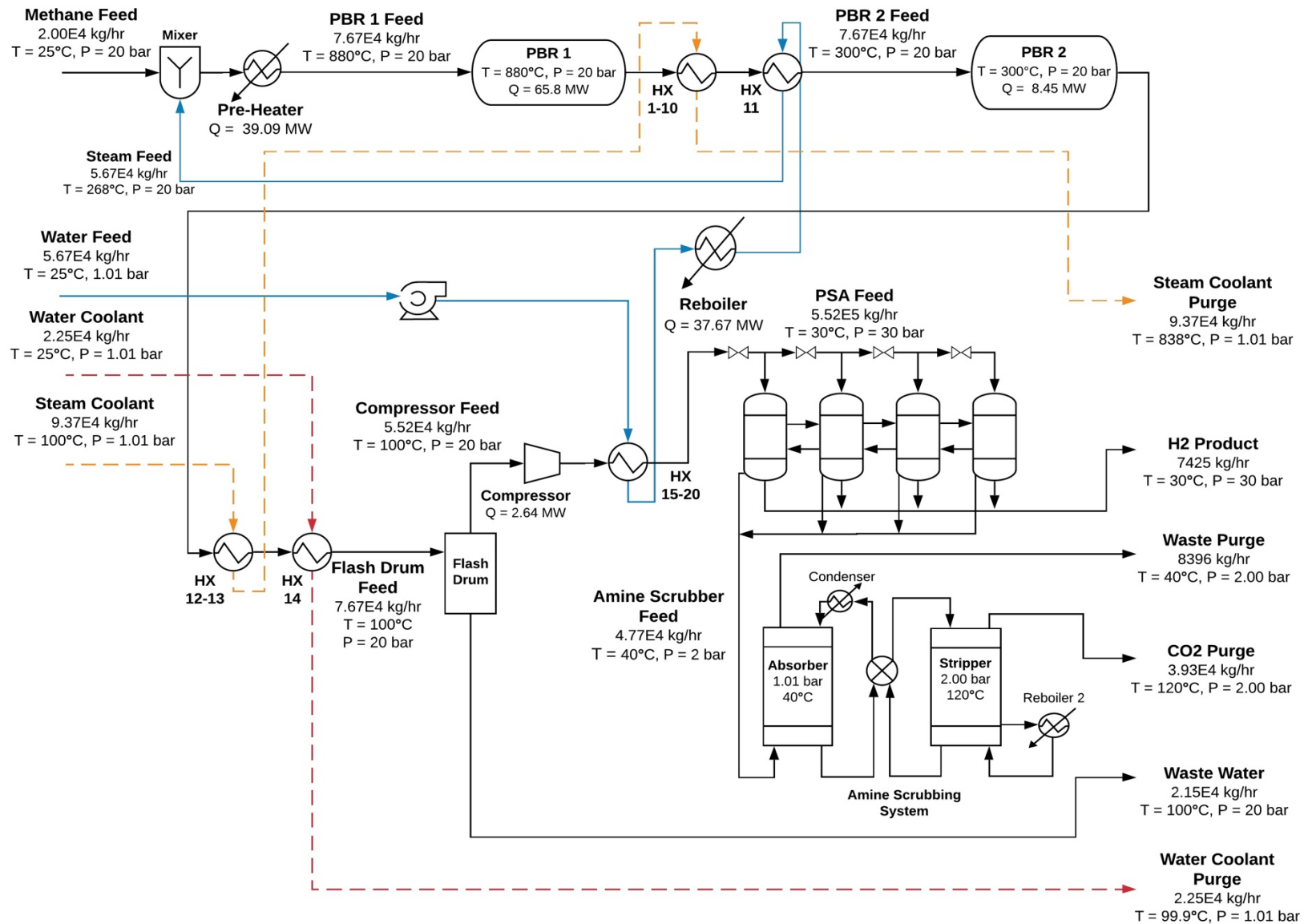
The main components of the plant design include: 2 PBRs placed in series, a flash drum, a gas compressor, a pressure swing adsorber (PSA), an amine scrubbing system, 3 furnaces, and a network of 20 total heat exchangers. The first reactor (PBR 1) has a volume of 93.6 m<sup>3</sup> and is filled with Ni-Mg catalyst that carries out the steam methane reforming reaction. The second reactor (PBR 2) has a volume of 104.8 m<sup>3</sup> and CZA catalyzes the water gas shift reaction. The selected volumes maximize conversion of limiting reactant at the chosen reactor temperatures.

In an effort to maximize heat integration, 11 heat exchangers, each with surface areas of 60.32 m<sup>2</sup>, are installed between the two reactors, effectively dropping the temperature from 880 to 300 °C while simultaneously heating the steam feed and lowering the costly heat duty consumed by the pre-reactor furnace. The 3 heat exchangers after the second PBR drop the temperature of the effluent stream to 100 °C, where H<sub>2</sub>O is condensed to a liquid and can be removed from the stream by the flash drum. A compressor is placed after the flash drum to increase the pressure of the remaining gas stream before entering the PSA. The final 6 heat exchangers drop the stream temperature to 30 °C to fit the requirements of the PSA, while partially vaporizing the liquid water feed that runs through the heat exchangers. The remainder of the water feed is then vaporized in the reboiler, and the gas stream enters the PSA at 30 bar and 30 °C. 90% of the hydrogen gas from the stream exits the PSA with a 0.99999 wt % purity at a pressure of 30 bar. The remainder of the gas stream that entered the PSA is sent to an amine separator, where 100% of the CO<sub>2</sub> is removed from the stream and sent away for sequestration.

Now, the other gas stream leaving the amine separator only contains CO, CH<sub>4</sub>, and H<sub>2</sub>, and is redirected to the three furnaces, where it is burned for thermal energy, reducing operational cost. The extra CO<sub>2</sub> from burning this stream, along with all CO<sub>2</sub> produced from other furnaces is accounted for in the total sequestration cost. A table accounting for all CO<sub>2</sub> produced is located in Appendix C.1.

The full process flow diagram (PFD) is shown in Fig. 3. Detailed conditions of each flow stream in the PFD are outlined in Table 2a, and all equipment specifications are located in Table 2b.





**Figure 3.** Process flow diagram of the proposed plant where water and methane are converted to produce 63 kta of high purity hydrogen gas.



**Table 1a.** Stream properties from HYSYS design of process.

Stream	Mass Flow Rate		Composition (mass %)					T (°C)	P (bar)
	kg/hr	MT/yr	CH <sub>4</sub>	H <sub>2</sub> O	CO	CO <sub>2</sub>	H <sub>2</sub>		
Methane Feed	2.00E+4	1.68E+5	99.0	0	0	0.8	0.2	25.0	20.0
Steam Feed	5.67E+4	4.76E+5	0	100	0	0	0	268	20.0
Water Feed	5.67E+4	4.76E+5	0	100	0	0	0	25.0	1.01
Mixer Effluent (2)	7.67E+4	6.44E+5	25.8	73.9	0	0.22	0.08	195	20.0
PBR 1 Feed	7.67E+4	6.44E+5	25.8	73.9	0	0.22	0.08	880	20.0
PBR 1 Effluent	7.67E+4	6.44E+5	3.63	46.3	34.7	6.68	8.72	880	20.0
PBR 2 Feed	7.67E+4	6.44E+5	3.63	46.3	34.7	6.68	8.72	300	20.0
PBR 2 Effluent	7.67E+4	6.44E+5	3.63	28.1	6.25	51.3	10.8	300	20.0
Flash Drum Feed	7.67E+4	6.44E+5	3.63	28.1	6.25	51.3	10.8	100	20.0
Compressor Feed	5.52E+4	4.64E+5	5.05	0	8.68	71.3	15.0	100	20.0
PSA Feed	5.52E+4	4.64E+5	5.05	0	8.68	71.3	15.0	30.0	30.0
H <sub>2</sub> Product	7425	6.23E+5	0	0	0	0	100	30.0	30.0
Amine Scrubber Feed	4.77E+4	4.00E+5	5.83	0	10.0	82.4	1.73	40.0	2.00
CO <sub>2</sub> Purge	3.93E+4	3.30E+5	0	0	0	100	0	120	2.00
Waste Purge	8396	7.05E+4	0.12	0	31.1	0	68.8	40.0	2.00
Water Coolant	2.25E+4	1.89E+5	0	100	0	0	0	25.0	1.01
Steam Coolant	9.37E+4	7.87E+5	0	100	0	0	0	100	1.01
Water Coolant Purge	2.25E+4	1.89E+5	0	100	0	0	0	99.9	1.01
Steam Coolant Purge	9.37E+4	7.87E+5	0	100	0	0	0	838	1.01

\*PBR = Packed Bed Reactor

PSA = Pressure Swing Adsorber

(2) = Stream labeled 2 in HYSYS flow diagram

**Table 1b.** Equipment parameters taken from HYSYS simulation of design process. For heat exchangers, the hot stream flows through the tube and the cold stream flows through the shell. Full heat exchanger system is shown in Appendix D.1

Equipment	Inlet T (°C)		Outlet T (°C)		Pressure In (bar)		Pressure Out (bar)		Vol (m <sup>3</sup> )	Duty (MW)
Heat Exchangers	Tube	Shell	Tube	Shell	Tube	Shell	Tube	Shell	Area (m <sup>2</sup> )	For HXs: heat transferred
HX-1	880	788	834	838	20.0	1.01	20.0	1.01	60.32	3.05
HX-2	834	734	785	788	20.0	1.01	20.0	1.01	60.32	3.23
HX-3	785	672	729	734	20.0	1.01	20.0	1.01	60.32	3.65
HX-4	729	604	667	672	20.0	1.01	20.0	1.01	60.32	4.00
HX-5	667	527	598	604	20.0	1.01	20.0	1.01	60.32	4.39
HX-6	598	439	520	527	20.0	1.01	20.0	1.01	60.32	4.89
HX-7	520	337	431	439	20.0	1.01	20.0	1.01	60.32	5.48
HX-8	431	243	350	337	20.0	1.01	20.0	1.01	60.32	4.90
HX-9	350	226	335	243	20.0	1.01	20.0	1.01	60.32	0.897
HX-10	335	220	330	226	20.0	1.01	20.0	1.01	60.32	0.299
HX-11	330	215	300	268	20.0	20.0	20.0	20.0	60.32	1.79
HX-12	300	160	250	220	20.0	1.01	20.0	1.01	60.32	3.03
HX-13	250	100	200	160	20.0	1.01	20.0	1.01	60.32	3.00
HX-14	200	25	100	99.9	20.0	1.01	20.0	1.01	60.32	15.8
HX-15	157	78.2	108	111	30.0	1.01	30.0	1.01	60.32	2.29
HX-16	108	56.4	76.0	78.2	30.0	20.0	30.0	20.0	60.32	1.49
HX-17	76.0	42.1	55.0	56.4	30.0	20.0	30.0	20.0	60.32	0.972
HX-18	55.0	33.3	42.0	42.1	30.0	20.0	30.0	20.0	60.32	0.599
HX-19	42.0	28.6	35.0	33.3	30.0	20.0	30.0	20.0	60.32	0.322
HX-20	35.0	25.2	30.0	28.6	30.0	20.0	30.0	20.0	60.32	0.230
Preheater	195		880		20.0		20.0		N/A	39.1
Reboiler	111		215		20.0		20.0		N/A	37.7
PBR 1	880		880		20.0		20.0		93.6	65.8

<b>PBR 2</b>	300	300	20.0	20.0	105	-8.
<b>Pump</b>	25.0	25.2	1.01	20.0	N/A	0.0395
<b>Compressor</b>	100	157	20.0	30.0	N/A	2.63
<b>Flash Drum</b>	100	100	20.0	20.0	N/A	N/A
<b>PSA</b>	30.0	30.0	30.0	30.00	N/A	0.117
<b>Amine Sep.</b>	40.0	120	2.00	2.00	N/A	0.890

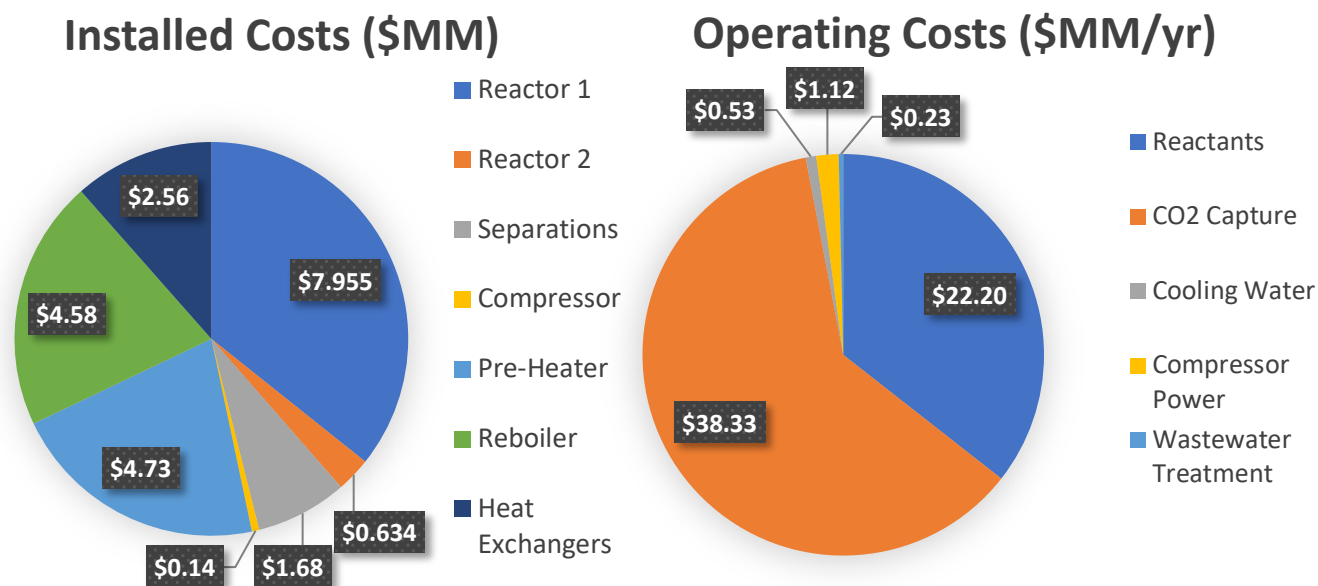
HX = Heat Exchanger      PBR = Packed-Bed Reactor      PSA = Pressure Swing Adsorber

### 3. Economic Analysis

#### 3.1 Equipment Costing and Specification

A technoeconomic cost analysis was carried out in order to evaluate the profitability and economic feasibility of our plant design. First, equipment configurations and conditions were varied in a process of trial and error. The HYSYS simulation with the greatest economic potential was used estimate cost. After confirming that the results from the simulation agreed with our MATLAB predictions, relevant parameters like reactor sizes and flow rates were recorded from HYSYS.

Next, these values were used to calculate installation and operating costs using Douglas's factored estimates [1]. Figures 4 and 5 summarize the cost breakdowns to help gain a better understanding of how expenses are weighed among all processes and equipment types.



**Figure 4.** Pie charts detailing installed costs and operating costs based on the individual price of each system component or process.

Reactor 1 takes up the largest share of installed costs as illustrated in Figure 4. This is because the installation of reactor 1 includes the furnace used to keep it at a constant temperature of 880 °C. The compressor installation cost is kept low due to the reactions running at 20 bar, lowering the compression ratio. Figure 5 shows that CO<sub>2</sub> capture is the largest expense at \$38.33 MM per year, which outweighs the feedstock price by a factor of 1.73. By implementing an integrated system of heat exchangers and choosing to burn

unreacted reactants we successfully eliminated all heating costs. That is why heating is not present in the operating cost breakdown. This was a crucial step in our effort to make up for the large cost of CO<sub>2</sub> sequestration that all other Hydrogen plants release into the atmosphere for free.

### 3.2 Discounted Cash Flow Analysis

A discounted cash flow sheet was created using the costing estimates from the base-case HYSYS operating conditions. Equipment installation costs were summed to determine an inside battery limits (ISBL) cost and working capital (WC) was assumed to be equal to two months of feedstock cost. Using factored estimates, initial total investment was estimated to be  $2.5 \times \text{ISBL} + \text{WC}$  and start up (SU) was determined to be  $2.28 \times \text{ISBL}$ . This total investment was divided over a 2-year construction time at a 6% interest rate, giving a final total investment (TI) of \$70 MM. This TI was then borrowed in the form of a 10-year bond with a fixed 4% interest rate. Fixed and variable costs were also determined from HYSYS and relevant economic parameters are summarized in Table 2.

**Table 2.** Summary of key economic cost estimates used to determine the TI needed in bond purchases. These values were found using the base-case HYSYS simulation.

Economic Parameter	Estimate of Required Capital [\$MM]
Working Capital (WC)	\$3.7
Start Up Capital (SU)	\$5.1
Total Fixed Capital (FC)	\$61.5
Annual Product Revenue	\$81.9
Annual Fixed Costs	\$8.2
Annual Variable Costs	\$62.4
<b>Total Investment (TI)</b>	<b>\$70.3</b>

After factoring in a 27% tax rate and a ten-year 10% depreciation discounted cash flow, NPV, NPV%, and Return on Investment (ROI) were calculated for the remaining 12 years of plant life. More detailed equations and a cash flow diagram can be found in appendices C.1 and C.2.

Our best case NPV was found to be \$10.8 MM with an IRR of 145% and an NPV% of 1.1%. IRR calculation can be found in Appendix C.3. Although the plant was able to achieve a positive NPV, NPV% and revenues are still too low to for potential investing. In order to better understand what the plant would need to be profitable, we calculated the minimum price that hydrogen would have to be in order to achieve an NPV% of 0% and a reasonable value of 10%. The minimum price of CO<sub>2</sub> sequestration to achieve 10 NPV% was calculated as well. Profitability measures for all four cases are shown in Table 3 below.

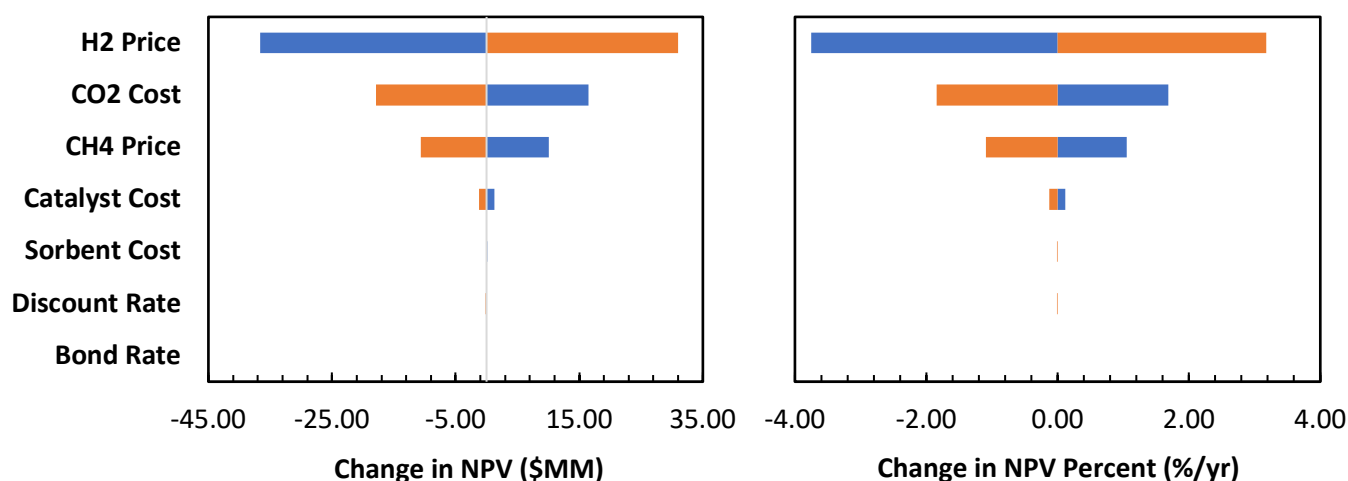
**Table 3.** Measures of profitability after 14 years when the sale price of hydrogen and sequestration cost of carbon dioxide are altered.

Condition	Price of H <sub>2</sub>	Measure of Profitability after 14 years		
		NPV [\$MM]	NPV%	Year 14 ROI
Regular Price	\$1,300/MT	\$10.81	1.11%	16.1%
Decreased price for 0 NPV%	\$1,259/MT	-\$0.04	0%	12.8%
Increased price for 10 NPV%	\$1,670/MT	\$97.66	10%	45.9%
CO <sub>2</sub> Sequestration cost decreased by 55%	\$91/MT (with N <sub>2</sub> ) \$45/MT (without N <sub>2</sub> )	\$97.57	10%	45.8%

Table 3 shows that a 28% increase in the price of hydrogen to \$1,670/MT was enough to raise the NPV% to 10%, while A 3% decrease in the price was enough to lower it to zero. It should be noted that profits were far more sensitive to the price of hydrogen than to that of CO<sub>2</sub> sequestration. A much larger 55% decrease in the cost of sequestration was needed to raise the NPV% to ten. Since hydrogen needs to be sold at \$1,670/MT to make an acceptable amount of profit, this value was used in further calculations to model the secondary distribution and sales system.

### 3.3 Sensitivity Analysis

Further sensitivity analysis was conducted by varying several parameters to see the influence that they had on profitability. Keeping other variables constant and assuming constant annual cost, the prices of hydrogen, methane, CO<sub>2</sub> and catalyst as well as the construction, discount and bond rate were both increased and decreased by 10%. Their effects on NPV and NPV% are shown in Figure 6 tornado charts below. As expected, the price of hydrogen and CO<sub>2</sub> capture had the largest effect on profit.



**Figure 6:** Tornado charts showing the response in NPV and NPV% to a ± 10% change in input variable. Calculations were made from the base-case HYSYS simulation.

There are a variety of scenarios that could be detrimental to profitability. Fossil fuels are prone to large fluctuations in price which would be unfavorable in the case that the price of methane feed goes up. Furthermore, Southern California is a very wealthy area. In the case that sustainable steam methane reforming does become profitable or socially supported, other competitive hydrogen producers could enter the market which would cause the price to decrease.

#### 4. Distribution and Sales System

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To estimate an appropriate retail selling price of hydrogen to pay at the filling station pump, we created a distribution model that utilizes gaseous truck trailer transportation. The distribution business was assumed to be a separate entity that would buy hydrogen gas from the plant at 30 bar for the 10 NPV% price of \$1670/MT.

First, the gas is compressed from 30 bar into transportation tanks at 250 bar, which is the maximum pressure allowed on a pressurized tank vehicle by the Department of Transportation. Then, the gas is trucked from the plant to one of the 35 refueling stations located along the 101 freeway between Santa Barbara and Los Angeles. Lastly, the gas needs to be recompressed at the station to the selling pressure of 700 bar.

The major costs of distribution come from compression, equipment capital, fuel, and labor. Twenty compressors were needed at the plant to accomplish the large duty of the first compression while each of the 35 refueling stations has its own personal compressor for the last compression. The average two-way drive distance of 124 miles accounts for the various station locations scattered between LA and Santa Barbara. Single truck carrying capacity was assumed to be 300 kg H<sub>2</sub> which is the standard value [6]. All other assumptions are listed in Appendix E.

All assumptions were incorporated to determine total number of trips per year, miles traveled per year, and delivery hours per year. These values were then used to calculate a TI of \$496 MM, which accounts for all capital purchase and installation costs. TI was financed by a 10-year bond at a 4% fixed bond rate. Assuming a 10% discount rate and 27% tax rate, a cash flow sheet was created to determine NPV and NPV% at the end of 12 years. Calculations as well as a complete discounted cash flow sheet are found in Appendix E.

The hydrogen retail price required to achieve a 10 NPV% was found to be \$6.49/kg H<sub>2</sub>. This value is less than half the typical H<sub>2</sub> price of \$14/kg. Moreover, if the distribution business were to buy the H<sub>2</sub> at the regular price of \$1300/MT, the retail price would be even smaller at \$6.03/kg. These prices would be highly competitive in the current hydrogen market. Gasoline, however, is still a cheaper fuel. Gasoline costs \$0.013/MJ which is slightly larger compared to \$6.49/kg or \$0.054/MJ for hydrogen. Although, our distribution business is able to sell hydrogen at a competitive rate, more technological developments are needed to make it competitive with traditional fossil fuels.

## 5. Health and Safety Considerations

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Snell Oil Company holds in highest regard the safety of our employees and the conservation of our surrounding environment and community. Every species used in the operation of this plant has hazards especially at high temperatures, pressures and flow rates. Any safety concerns with our preliminary plant design have been analyzed and outlined in this report.

In terms of risk, the most major concern of plant operation is explosions/fire.  $H_2$ ,  $CH_4$ , and CO are all extremely flammable and can explode at high temperature conditions of the plant. The second PBR contains an exothermic reaction which poses another explosive risk as a runaway reaction could occur. The effluent stream has a high concentration of hydrogen, which has an auto ignition temperature range of 500-571°C. and a large explosive limit range of 4-75% by volume [7]. A leak to atmospheric pressure could result in either auto-ignition or an explosion. CO also has a large explosive limit of 5-15% and an auto-ignition temperature of 607°C and poses a threat as it exits PBR 1 at 880°C at its flow rate throughout the process [8]. Methane has an auto-ignition temperature of 537°C and an explosive limit of 5-15% but is less likely to cause an explosion since it reacts almost completely in PBR 1 [9].

To ensure potential explosive and flammable hazards are prevented, all plant equipment should be regularly checked and adequately maintained to prevent leaks or unit wear from causing a plant explosion. The cooling systems in place around high temperature units should also be maintained regularly. Pressure build up due to any systems failure could also lead to an explosion as the gas builds up within a closed space. Therefore, all feed valves should be fail-close so the streams throughout the plant stop flowing.

Another possible hazard is toxicity. Carbon monoxide is not only flammable but also an extremely poisonous gas with an exposure limit of 25 ppm and 8-hour time-weighted average [10]. In case of a leak, all employees should be wearing protective clothing, gloves, and a respirator.

Other general safety design features include burning the gas purge off site to keep an oxygen rich combustion reaction away from the plant. There should be adequate spacing between reactors and heat exchangers to prevent heating by convection. A process control system should control feed rates with fail close valves by measuring temperatures in all reactors and heat exchangers via thermocouples. If a unit becomes too hot, the system should release more coolant or close the valve in case of failure. Finally, while all the gaseous species are not very corrosive, all equipment should be made of stainless steel to prevent water corrosion.

## 6. Process Alternatives and Future Considerations

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Alternative designs do exist that were considered but ultimately dismissed for our current design. One alternative would be to recycle the water purge stream from the flash drum back into the mixer and feed it back into PBR 1. This stream is already at 20 bar and at 100°C and would not require a pump to pressurize it before being recycled into the mixer. This would theoretically eliminate the cost of wastewater disposal and require purchasing less process water. We did not recycle our water purge because the flow rate of the reactant water feed would have to decrease; otherwise, there would be too much water entering the reactors which would not only affect reactor conversion but also would cause fractional conversion errors within the heat exchangers. If the flow rate of the water feed were decreased, there is not enough coolant available to cool PBR 1's effluent and there would be a temperature cross within the heat exchangers. However, a different design of heat exchangers and cooling systems that would accommodate the desired temperature change could end up saving operational costs.

## 7. Conclusions

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With the current preliminary design and the prices of feedstocks and product, the proposed hydrogen plant will not be a profitable business venture to invest in. When the price of hydrogen is \$1300/MT, the maximum NPV value we can achieve is \$10.1 million. While this does not completely satisfy the needs of Snell Oil Company, more options may be explored for sustainable hydrogen fuel production. By increasing the price of our hydrogen product by 28%, the plant achieves an NPV<sub>%</sub> of 10% with a 45.9% ROI at year 14. We recommend advertising a higher price for the carbon-neutral hydrogen product, which will shift the economics in our favor and yield a positive NPV and large profits for the company.



## 8. References

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## 9. Appendix

### Appendix A: Physical Properties and Costs

	Methane	Water	Carbon Monoxide	Hydrogen	Carbon Dioxide	Mg/Ni catalyst	CZA catalyst
Physical State	Gas	Gas	Gas	Gas	Gas	Solid	Solid
Molecular Weight (g/mol)	16.04	18.02	28.01	2.016	44.01	N/A	N/A
Boiling Point (°C)	-161.5	100.0	-191.5	-252.9	-78.50	N/A	N/A
Density (kg/m <sup>3</sup> )	0.6560	1000.	1.140	0.08988	1.980	2000.	
Bulk Density (kg/m <sup>3</sup> )	N/A	N/A	N/A	N/A	N/A	1000	1000
Particle Diameter (m)	N/A	N/A	N/A	N/A	N/A	5.00E-3	5.00E-3

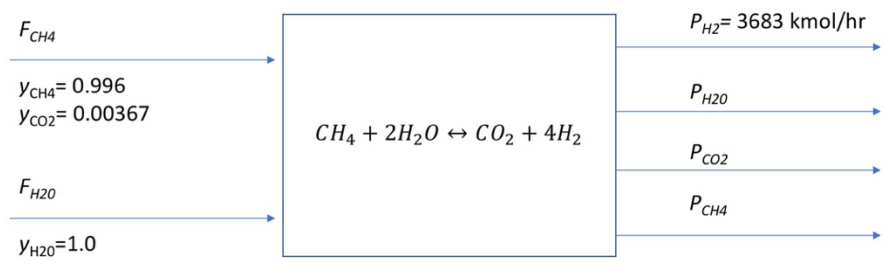
### Appendix B: Mole Balances

#### Methane Feed Mole Fractions

$$y_i = \frac{w_i / MW_i}{\sum w_i / MW_i}$$

Where  $w_i$  is the weight fraction and  $MW_i$  is the molecular weight of the species

#### Level 2 Mole Balance



#### H<sub>2</sub> Mole Balance

$$y_{H_2} * F_{CH_4} - y_{H_2} * P_{H_2} + v_{H_2} * y_{CH_4} * F_{CH_4} - 0 = 0$$

$$-3683 \frac{\text{kmol}}{\text{hr}} + 4(0.996 * F_{CH_4}) = 0$$

$$F_{CH_4} = 924.4 \frac{\text{kmol}}{\text{hr}}$$

#### H<sub>2</sub>O Mole Balance

$$y_{H_2O} * F_{H_2O} - 0 + 0 + v_{H_2O} * y_{CH_4} * F_{CH_4} = 0$$

$$1.0 * F_{H_2O} = 2 * 0.996 * 924.4 \frac{kmol}{hr}$$

$$F_{H_2O} = 1841 \frac{kmol}{hr}$$

### CO<sub>2</sub> Mole Balance

$$y_{CO_2} * F_{CH_4} - y_{CO_2} * P_{CO_2} + v_{CO_2} * y_{CH_4} * F_{CH_4} - 0 = 0$$

$$0.00367 * 924.4 \frac{kmol}{hr} - 1.0 * P_{CO_2} + 1 * 0.996 * 924.4 \frac{kmol}{hr} = 0$$

$$P_{CO_2} = 924.1 \frac{kmol}{hr}$$

### Pressure Drop

Ergun Equation

$$\frac{P}{P_0} = \left(1 - \frac{2\beta z}{P_0}\right)^{1/2}$$

$$\beta = \frac{G(1-\Phi)}{g_c \rho_0 D_p \Phi^3} \left[ \frac{150(1-\Phi)\mu}{D_p} + 1.75G \right]$$

$P/P_0$  is the ratio between the final and initial pressures,  $z$  is reactor length  $v$  is the total volumetric flow rate,  $\rho_0$  is the gas density,  $g_c$  is a conversion factor,  $D_p$  is the catalyst particle diameter,  $\Phi$  is the void fraction (void volume/total bed volume) and  $\mu$  is the gas viscosity.

### Reaction Kinetics



$$r_1 = \frac{1}{(p_{H_2} + \epsilon)^{2.5} \Psi^2} (k_1 p_{CH_4} p_{H_2O} - k_{-1} p_{H_2}^3 p_{CO}) \quad (4)$$

$$r_2 = \frac{1}{(p_{H_2} + \epsilon) \Psi^2} (k_2 p_{CO} p_{H_2O} - k_{-2} p_{H_2} p_{CO}) \quad (5)$$

$$r_3 = \frac{1}{(p_{H_2} + \epsilon)^{3.5} \Psi^2} (k_3 p_{CH_4} p_{H_2O}^2 - k_{-3} p_{H_2}^4 p_{CO}) \quad (6)$$

$$r_4 = k_4 p_{CO} p_{H_2O} - k_{-4} p_{H_2} p_{CO_2} \quad (7)$$

$$\Psi = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2} + \epsilon} \quad (8)$$

### Parameters in Arrhenius equation form

$$k = A e^{-E_a/RT} \quad (9)$$

$$k_1 = 2.50 * 10^{12} * \exp\left(-\frac{240.1}{RT}\right) \quad (10)$$

$$k_{-1} = 0.209 * \exp\left(-\frac{17.10}{RT}\right) \quad (11)$$

$$k_2 = 1.17 * 10^3 * \exp\left(-\frac{67.13}{RT}\right) \quad (12)$$

$$k_{-2} = 6.62 * 10^4 * \exp \left( -\frac{103.7}{RT} \right) \quad (13)$$

$$k_3 = 6.03 * 10^{11} * \exp \left( -\frac{243.9}{RT} \right) \quad (14)$$

$$k_{-3} = 2.85 * 10^5 * \exp \left( -\frac{57.40}{RT} \right) \quad (15)$$

$$k_4 = 1.31 * 10^{-2} * \exp \left( -\frac{15.43}{RT} \right) \quad (16)$$

$$k_{-4} = 0.740 * 10^5 * \exp \left( -\frac{52.01}{RT} \right) \quad (17)$$

$$K_{CO} = 8.250 * 10^{-5} * \exp \left( \frac{70.65}{RT} \right) \quad (18)$$

$$K_{H_2} = 6.150 * 10^{-9} * \exp \left( \frac{82.90}{RT} \right) \quad (19)$$

$$K_{CH_4} = 6.660 * 10^{-4} * \exp \left( \frac{38.28}{RT} \right) \quad (20)$$

$$K_{CO} = 1.765 * 10^5 * \exp \left( -\frac{88.68}{RT} \right) \quad (21)$$

# Appendix C: Economic Analysis

## C.1 Detailed Operating Costs and Installed Equipment

Operational Costs
-------------------

Product (H2) Profit		
Flow out [kta]	Price H2 \$/MT	Profit \$/yr
63	1300	\$81,900,000

Cost of Natural Gas Feed			Cost of Feed Water			Cost of CO2 Capture					Catalyst Cost		
Feed in [kg/hr]	Price CH4 \$/MT	Cost \$/yr	Feed in [kgmol/h]	Price \$/MT	Cost \$/yr	Flow out w N2 [mol/s]	Price to Sequester w N2 \$/MT	Flow out no N2 [mol/s]	Price to Sequester no N2 \$/MT	Cost \$/yr	Cat Weight [MT]	Price \$/MT	Cost \$/charge
2.00E+04	132	\$22,176,000	3150	0.05	\$23,827	2.00E+01	200	248.1	100	\$38,331,433	198.6	30000	\$5,958,000

Reactor 2 Cooling Water			Cooling Water for HX-14			Cooling Steam Cost for HX-(1-10, 12-13)			Wastewater Treatment Cost		
Q_out [kW]	Price \$/GJ	Cost \$/yr	Flow rate [kgmol/h]	Price \$/MT	Cost \$/yr	Flow rate [kgmol/h]	Price \$/MT	Cost \$/yr	Flow rate [kgmol/h]	Price \$/MT	Cost \$/yr
8450	2	\$511,056	1250	0.08	\$15,128	5205	2	\$1,574,866	1194	1.25	\$225,791

Cost to Power Compressor/Pump			Cost to Power Heaters Before Discount				Energy and CO2 Balance from Burning Excess Gas						
Power [MW]	Price [\$ /MW-h]	Cost [\$ /yr]		Q [W]	Price [\$ /MW-h]	Cost [\$ /yr]	Component	Flow Rate [mol/s]	Heat of Combustion [J/mol]	Energy Produced [W]	Energy Needed [W]	CO2 Produced After Discount [mol/s]	Thermal Cost After Discount [\$ /yr]
2.67	50	\$1,119,678	Feed Pre-Heater	3.91E+07	10	3283560	H2	7.95E+02	286000	2.27E+08	N/A	0.00E+00	N/A
			Reactor 1 Heater	6.58E+07	10	5.53E+06	CH4	4.11E-01	890000	3.65E+05	N/A	2.49E-01	N/A
			Reboiler	37670000	10	3.16E+06	CO	25.8678	294000	7.61E+06	N/A	1.57E+01	N/A
							Total	8.21E+02	2.87E+05	2.35E+08	1.43E+08	1.59E+01	0.00E+00

Electricity Audit				
Compressor Power Consumed [W]	Pump Power Consumed [W]	Conversion [kg CO2/kWh]	CO2 Produced using Electricity [kg/yr]	CO2 Produced [mol/s]
2630000	39500	0.2395	5370500.1	4.035353392

### Fixed Costs

Reactor Installation Costs							PSA					
	D [ft]	H [ft]	Fm	Fp	Fc	Cost [\$]	Cylinder Vol [m^3]	Fc	D [ft]	H [ft]	Cost of one PSA[\$]	Total Cost [\$]
Reactor 1 - Reformer	7.49	74.93	1	1.16	1.16	\$591,413	32	1	7.11	28.45	\$316,382	\$1,676,727
Reactor 2 - WGS	7.78	77.76	1	1.16	1.16	\$634,119	Mass Sorbent [kg]	Price of Sorbent [\$/kg]	Cost of Sorbent for one PSA [\$]			
							20560	5	\$102,800			

Compressor Installation Cost							Cost of Heat Exchanger Installation																											
Flow in [mol/s]	Efficiency	P_in [bar]	P_out [bar]	BHP	Fc	Cost[\$]		Area [ft^2]	Cost [\$]																									
1619	0.85	20	30	25.58340119	1	\$135,370	HE-1	649	\$128,176																									
<table><tr><th colspan="5">Cost to Install Heaters and Furnaces</th></tr><tr><th></th><th>Duty [W]</th><th>Duty [MM BTU/h]</th><th>Fc</th><th>Cost [\$]</th></tr><tr><td>Feed Pre-Heater</td><td>39090000</td><td>133.4</td><td>1</td><td>\$4,727,204</td></tr><tr><td>Reactor 1 Heater</td><td>65840000</td><td>224.6</td><td>1</td><td>\$7,363,171</td></tr><tr><td>Reboiler</td><td>37670000</td><td>128.5</td><td>1</td><td>\$4,580,837</td></tr></table>							Cost to Install Heaters and Furnaces						Duty [W]	Duty [MM BTU/h]	Fc	Cost [\$]	Feed Pre-Heater	39090000	133.4	1	\$4,727,204	Reactor 1 Heater	65840000	224.6	1	\$7,363,171	Reboiler	37670000	128.5	1	\$4,580,837	HE-2	649	\$128,176
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							HE-4	649	\$128,176																									
							HE-5	649	\$128,176																									
							HE-6	649	\$128,176																									
							HE-7	649	\$128,176																									
							HE-8	649	\$128,176																									
							HE-9	649	\$128,176																									
							HE-10	649	\$128,176																									
							HE-11	649	\$128,176																									
							HE-12	649	\$128,176																									
							HE-13	649	\$128,176																									
							HE-14	649	\$128,176																									
							HE-15	649	\$128,176																									
							HE-16	649	\$128,176																									
							HE-17	649	\$128,176																									
HE-18	649	\$128,176																																
HE-19	649	\$128,176																																
HE-20	649	\$128,176																																
Total IC HE 1-20 [\$] =								\$2,563,517																										

## C.2 DCF Sheet Used to Determine TCI, NPV, NPV%, and ROI

Profit was calculated assuming the regular hydrogen price of \$1300/MT.

<b>Discount rate</b>	10%
<b>Construction Rate</b>	6%
<b>Plant Tax Rate</b>	27%
<b>Bond Rate</b>	4%

<b>ISBL [MM\$]</b>	<b>\$22.27</b>
<b>Working Capital [MM\$]</b>	<b>\$3.70</b>
<b>Product Revenue [MM\$/yr]</b>	<b>\$81.90</b>
<b>Fixed Costs [MM\$/yr]</b>	<b>\$8.19</b>
<b>Variable Costs [MM\$/yr]</b>	<b>\$62.40</b>
<b>Catalyst Cost [MM\$/yr]</b>	<b>\$5.96</b>
<b>Initial TI [MM\$]</b>	<b>\$59.38</b>
<b>Start Up Capital [MM\$]</b>	<b>\$5.08</b>

[illegible]



Allowed Depreciation [MM\$]	Taxable Earnings [MM\$]	Taxes Paid [MM\$]	After Tax Profit [MM\$]	Cash Flow [MM\$]	DF	DCF Discounted Cash Flow [MM\$]	NPV [MM\$]	NPV%	Pre-tax ROI [%]
				0.00	1.00	0.00	0.00	0%	
				0.00	0.91	0.00	0.00	0%	
				0.00	0.83	0.00	0.00	0%	
6.66	-1.31	0.00	5.35	2.54	0.75	1.91	1.91	0.90%	7.6%
6.66	4.65	1.25	10.05	7.24	0.68	4.95	6.85	2.44%	16.1%
6.66	4.65	1.25	10.05	7.24	0.62	4.50	11.35	3.23%	16.1%
6.66	-1.31	0.00	5.35	2.54	0.56	1.43	12.78	3.03%	7.6%
6.66	4.65	1.25	10.05	7.24	0.51	3.72	16.49	3.35%	16.1%
6.66	4.65	1.25	10.05	7.24	0.47	3.38	19.87	3.53%	16.1%
6.66	-1.31	0.00	5.35	2.54	0.42	1.08	20.95	3.31%	7.6%
6.66	4.65	1.25	10.05	7.24	0.39	2.79	23.74	3.38%	16.1%
6.66	4.65	1.25	10.05	7.24	0.35	2.54	26.28	3.40%	16.1%
6.66	-1.31	0.00	5.35	-67.78	0.32	-21.60	4.68	0.55%	7.6%
0.00	11.31	3.05	8.25	8.25	0.29	2.39	7.07	0.77%	16.1%
0.00	11.31	3.05	8.25	8.25	0.26	2.17	9.24	0.94%	16.1%
				3.70	0.26	0.97	10.22	1.10%	
	3.08	0.83	2.25	2.25	0.26	0.59	10.81	1.11%	

<b>NPV [MM\$] =</b>	<b>\$10.81</b>
<b>NPV% =</b>	<b>1.11%</b>
<b>TCI [MM\$] =</b>	<b>\$65.24</b>
<b>Year 14 ROI =</b>	<b>16.1%</b>

### C.3 DCF Sheet Used to determine IRR

<b>Discount rate</b>	145%
<b>Construction Rate</b>	6%
<b>Plant Tax Rate</b>	27%
<b>Bond Rate</b>	4%

<b>ISBL [MM\$]</b>	22.3
<b>Working Capital [MM\$]</b>	3.7
<b>Product Revenue [MM\$/yr]</b>	81.9
<b>Fixed Costs [MM\$/yr]</b>	8.19
<b>Variable Costs [MM\$/yr]</b>	62.4
<b>Catalyst Cost [MM\$/yr]</b>	6.0
<b>Initial TI [MM\$]</b>	59.4
<b>Start Up Capital [MM\$]</b>	5.1

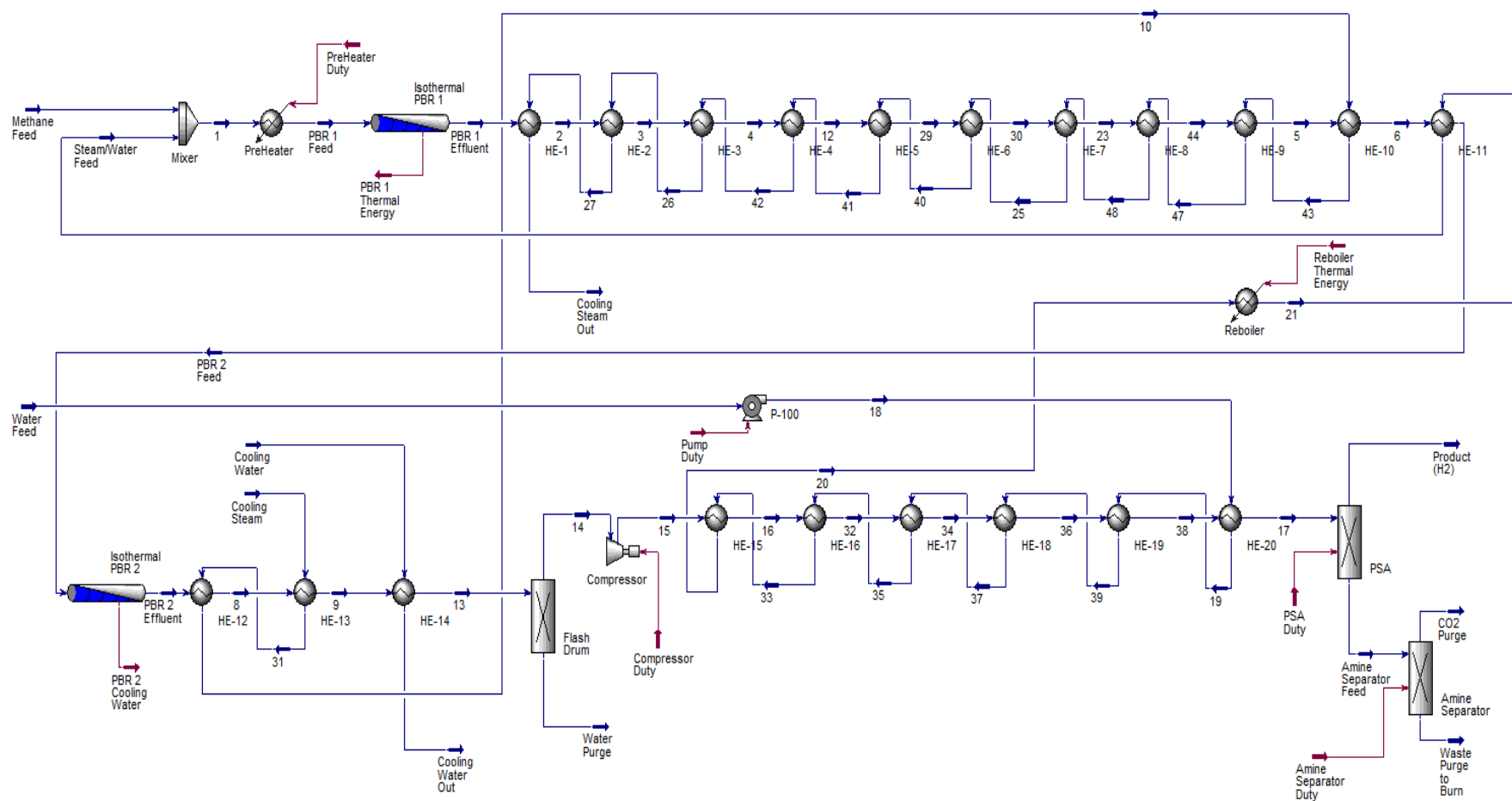
End of year	Annual Project Expenses [MM\$]	Interest on Construction Loan [MM\$]	Total Fixed Capital FC [MM\$]	Working Capital [MM\$]	Total Capital Investment TCI [MM\$]	Start-Up Capital [MM\$]	Total Investment [MM\$]	10 yr Bond Financing [MM\$]	Total Gross Revenue from Sale of Product [MM\$]	Cost of Catalyst every 3 years [MM\$]	Total Fixed Cost of Production [MM\$]	Total Variable Cost of Production [MM\$]	EBITDA Gross Earnings Cost of Production [MM\$]
0	5.94		5.94		5.94		5.94						
1	23.75	0.36	30.05		30.05		30.05						
2	29.69	1.80	61.54	3.70	65.24	5.08	70.32	70.32					
3								2.81	81.90	5.96	14.15	62.40	5.35
4								2.81	81.90	0.00	8.19	62.40	11.31
5								2.81	81.90	0.00	8.19	62.40	11.31
6								2.81	81.90	5.96	14.15	62.40	5.35
7								2.81	81.90	0.00	8.19	62.40	11.31
8								2.81	81.90	0.00	8.19	62.40	11.31
9								2.81	81.90	5.96	14.15	62.40	5.35
10								2.81	81.90	0.00	8.19	62.40	11.31
11								2.81	81.90	0.00	8.19	62.40	11.31
12					Bond Payoff		70.32	2.81	81.90	5.96	14.15	62.40	5.35
13	Salvage Value =								81.90	0.00	8.19	62.40	11.31
14									81.90	0.00	8.19	62.40	11.31
14													
14	WC =		3.08										3.08

Allowed Depreciation [MM\$]	Taxable Earnings [MM\$]	Taxes Paid [MM\$]	After Tax Profit [MM\$]	Cash Flow [MM\$]	DF	DCF Discounted Cash Flow [MM\$]	NPV [MM\$]
				0.00	1.00	0.00	0.00
				0.00	0.41	0.00	0.00
				0.00	0.17	0.00	0.00
6.66	-1.31	0.00	5.35	2.54	0.07	0.17	0.17
6.66	4.65	0.00	11.31	8.49	0.03	0.24	0.41
6.66	4.65	0.00	11.31	8.49	0.01	0.10	0.50
6.66	-1.31	0.00	5.35	2.54	0.00	0.01	0.52
6.66	4.65	0.00	11.31	8.49	0.00	0.02	0.53
6.66	4.65	0.00	11.31	8.49	0.00	0.01	0.54
6.66	-1.31	0.00	5.35	2.54	0.00	0.00	0.54
6.66	4.65	0.00	11.31	8.49	0.00	0.00	0.54
6.66	4.65	0.00	11.31	8.49	0.00	0.00	0.54
6.66	-1.31	0.00	5.35	-67.78	0.00	0.00	0.54
0.00	11.31	3.05	8.25	8.25	0.00	0.00	0.54
0.00	11.31	3.05	8.25	8.25	0.00	0.00	0.54
				3.70	0.00	0.00	0.54
	3.08	0.83	2.25	2.25	0.00	0.00	<b>0.54</b>

**IRR = 145%**

NPV [MM\$] = \$ 0.5

## Appendix D: Additional Figures



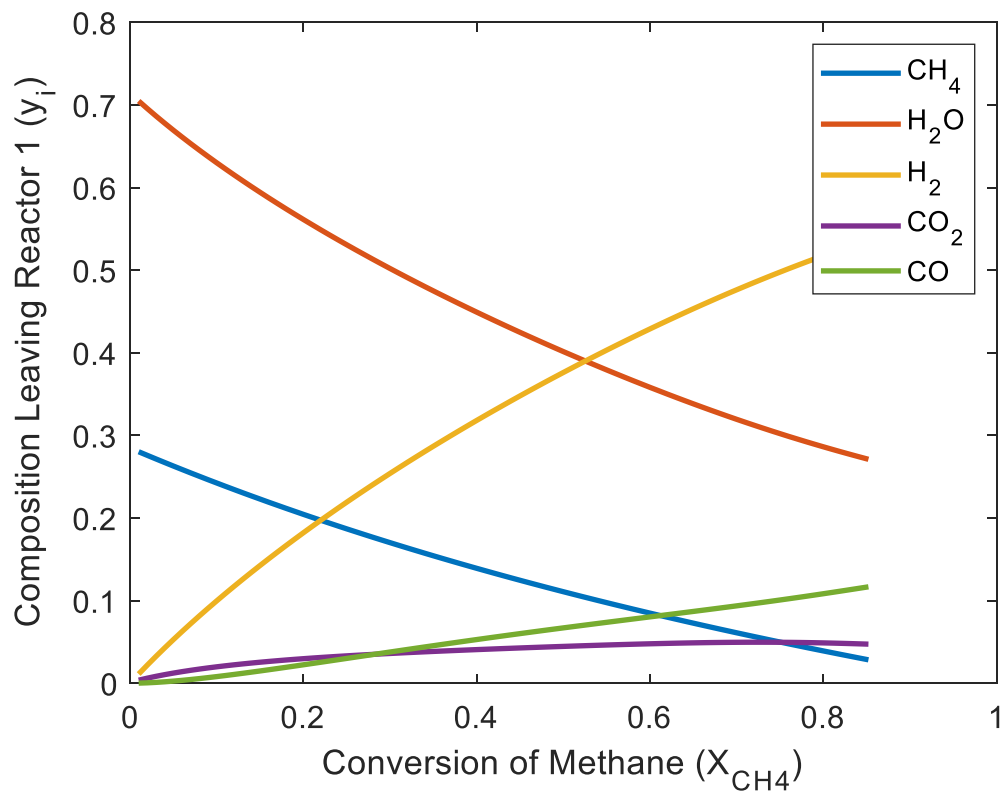
**Figure D.1.** HYSYS Process Flow Diagram with complete heat exchanger system.

**Table D.1** Stream table from conceptual design with design variables of key streams.

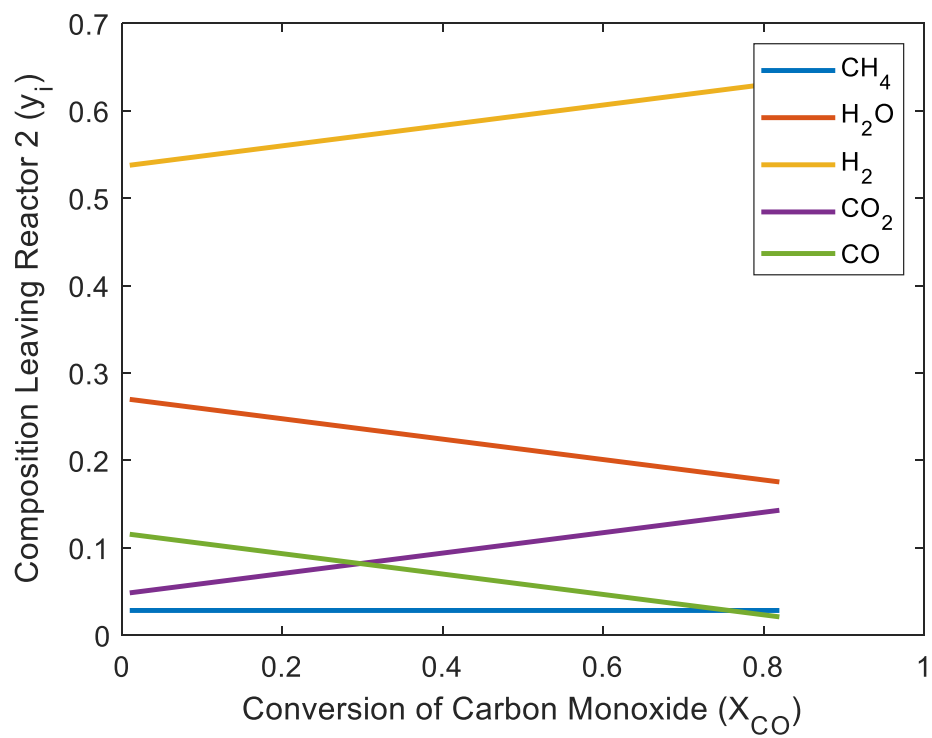
Stream	Mass Flow Rate		Composition (mass %)					T (°C)	P (bar)
	kg/hr	MT/yr	CH <sub>4</sub>	H <sub>2</sub> O	CO	CO <sub>2</sub>	H <sub>2</sub>		
Methane Feed	2.031E+4	1.71E+5	99.0	0	0	1.00	0	880.0	20.0
Steam Feed	5.66E+4	4.75E+5	0	100	0	0	0	880.0	20.0
PBR 1 Feed	7.69E+4	6.46E+5	26.1	73.6	0	0.27	0	880.0	20.0
PBR 1 Effluent	7.69E+4	6.46E+5	3.87	41.5	27.8	17.7	9.2	880.0	20.0
PBR 2 Feed	7.69E+4	6.46E+5	3.87	41.5	27.8	17.7	9.2	300.0	20.0
PBR 2 Effluent	7.69E+4	6.46E+5	3.87	26.8	5.01	53.5	10.8	300.0	20.0
Compressor Feed	5.63E+4	4.73E+5	5.3	0	6.8	73.1	14.8	100.0	20.0
PSA Feed	5.63E+4	4.73E+5	5.3	0	6.8	73.1	14.8	30.0	30.0
H <sub>2</sub> Product	7497	6.30E+5	0	0	0	0	100	30.0	30.0
CO <sub>2</sub> Purge	4.11E+4	3.46E+5	0	0	0	100	0	30.0	2.0

**Table D.1** Stream comparison of conceptual vs HYSYS designs. **Blue** values represent parameters from HYSYS

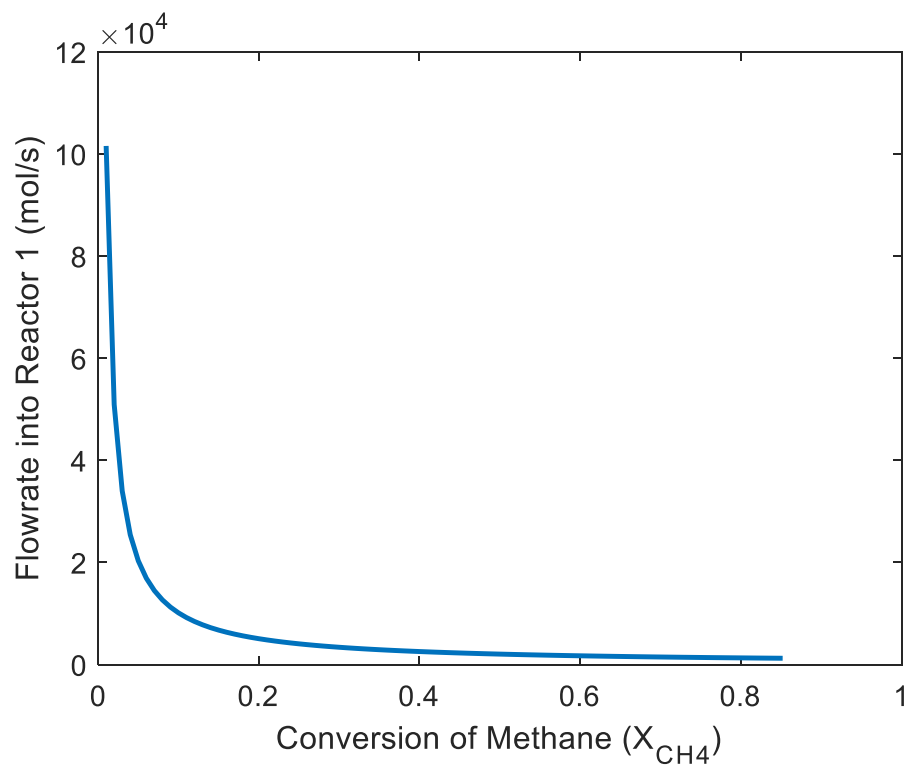
Stream	Mass Flow Rate		Composition (mass %)					T (°C)	P (bar)
	kg/hr	MT/yr	CH <sub>4</sub>	H <sub>2</sub> O	CO	CO <sub>2</sub>	H <sub>2</sub>		
Methane Feed	2.031E+4	1.71E+5	99.0	0	0	1.00	0	880	20.0
	2.00E+4	1.68E+5	99.0	0	0	0.80	0.20	25.0	20.0
Steam Feed	5.66E+4	1.30E+6	0	100	0	0	0	880	20.0
	5.67E+4	4.76E+5	0	100	0	0	0	268	20.0
PBR 1 Feed	7.69E+4	6.46E+6	26.1	73.6	0	0.27	0	880	20.0
	7.67E+4	6.44E+5	25.8	73.9	0	0.22	0.08	880	20.0
PBR 1 Effluent	7.69E+4	6.46E+6	3.87	41.5	27.8	17.7	9.2	880	20.0
	7.67E+4	6.44E+5	3.63	46.3	34.7	6.68	8.72	880	20.0
PBR 2 Feed	7.69E+4	6.46E+6	3.87	41.5	27.8	17.7	9.2	300	20.0
	7.67E+4	6.44E+5	3.63	46.3	34.7	6.68	8.72	300	20.0
PBR 2 Effluent	7.69E+4	6.46E+6	3.87	26.8	5.01	53.5	10.8	300	20.0
	7.67E+4	6.44E+5	3.63	28.1	6.25	51.3	10.8	300	20.0
Compressor Feed	5.63E+4	4.73E+5	5.3	0	6.8	73.1	14.8	100	20.0
	5.52E+4	4.64E+5	5.05	0	8.68	71.3	15.0	100	20.0
PSA Feed	5.63E+4	4.73E+5	5.3	0	6.8	73.1	14.8	30.0	30.0
	5.52E+4	4.64E+5	5.05	0	8.68	71.3	15.0	30.0	30.0
H <sub>2</sub> Product	7497	6.30E+5	0	0	0	0	100	30.0	30.0
	7425	6.23E+5	0	0	0	0	100	30.0	30.0
CO <sub>2</sub> Purge	4.11E+4	3.46E+5	0	0	0	100	0	30.0	2.0
	3.93E+4	3.30E+5	0	0	0	100	0	120	2.0



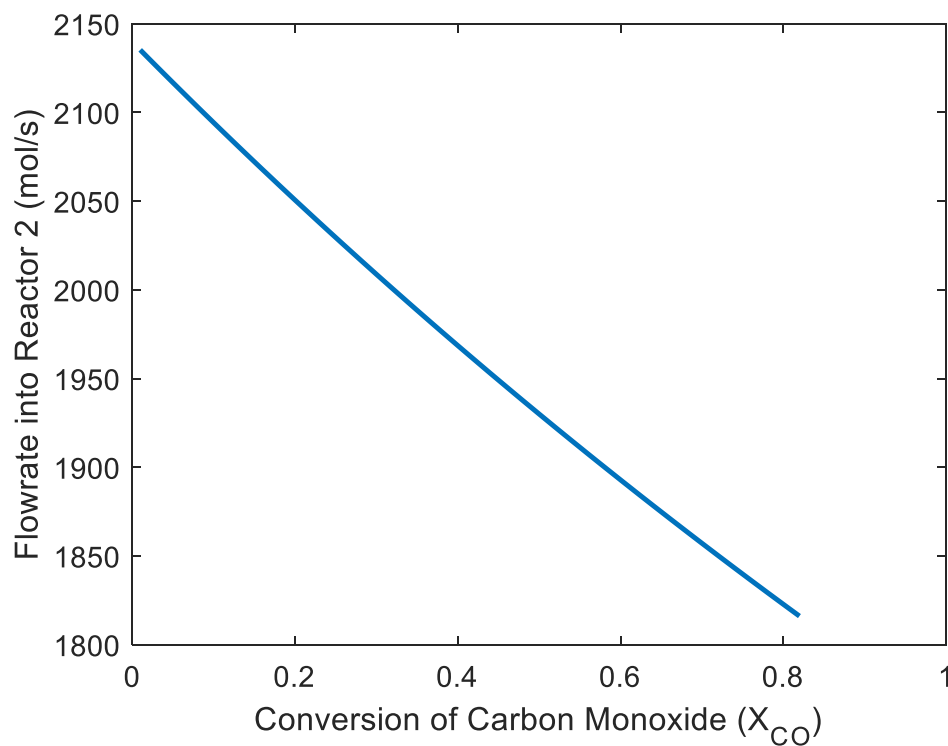
**Figure D.1** Composition of stream leaving reactor 1 versus conversion of  $CH_4$  in reactor 1



**Figure D.2** Composition of stream leaving reactor 2 versus conversion of  $CO$  in reactor 2

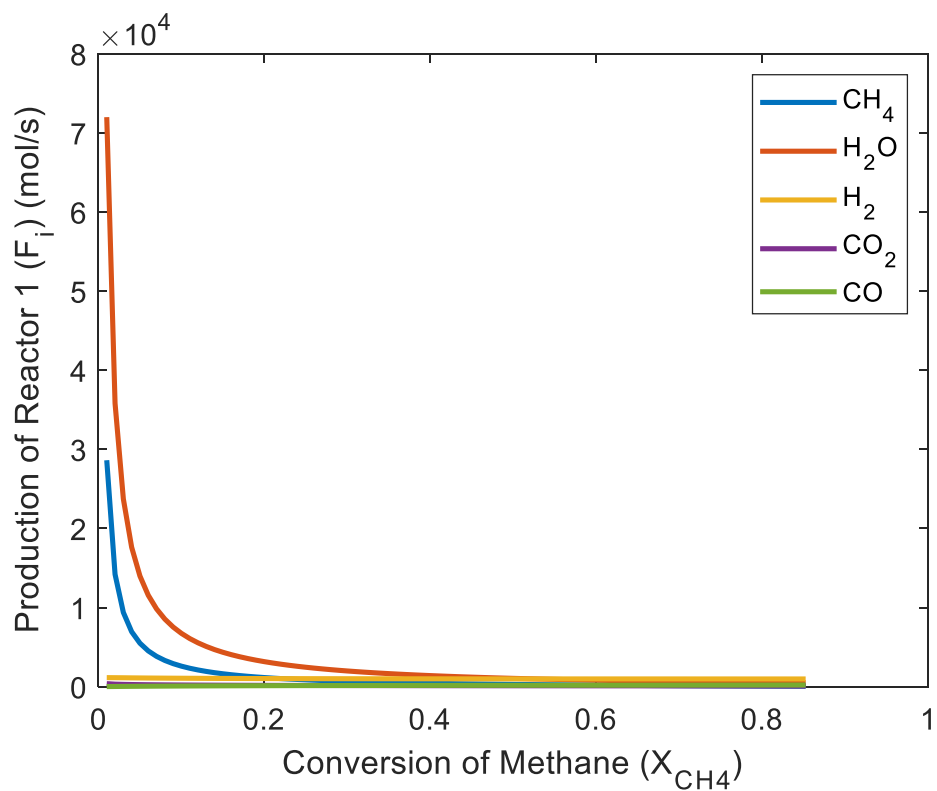


**Figure D.3** Flowrate into reactor 1 versus conversion of  $CH_4$  in reactor 1

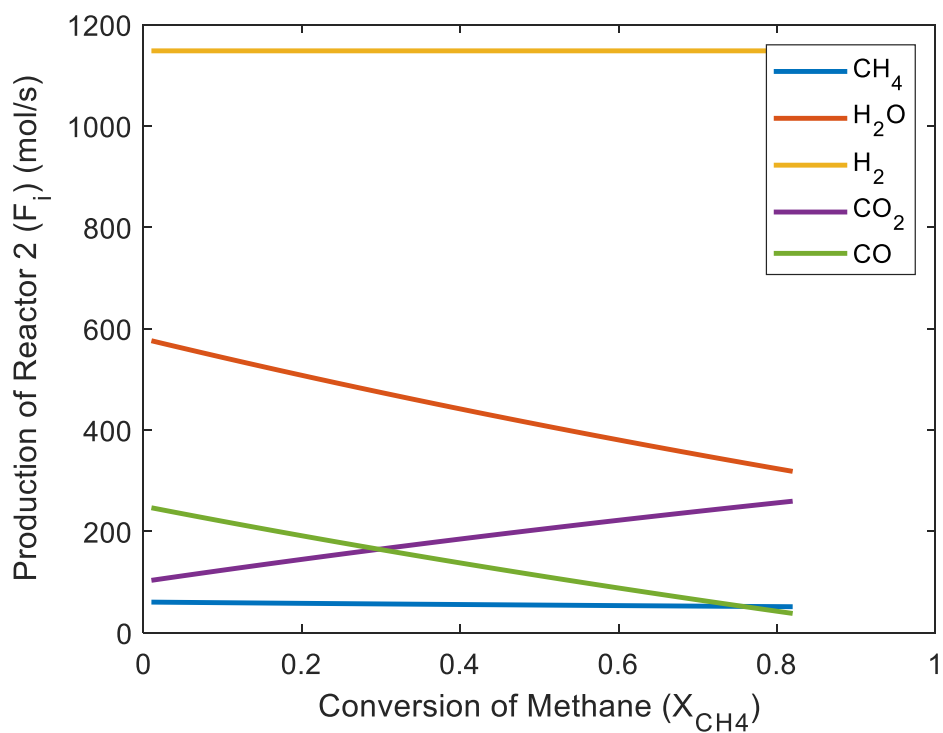


**Figure D.4** Flowrate into reactor 2 versus conversion of  $CO$  in reactor 2

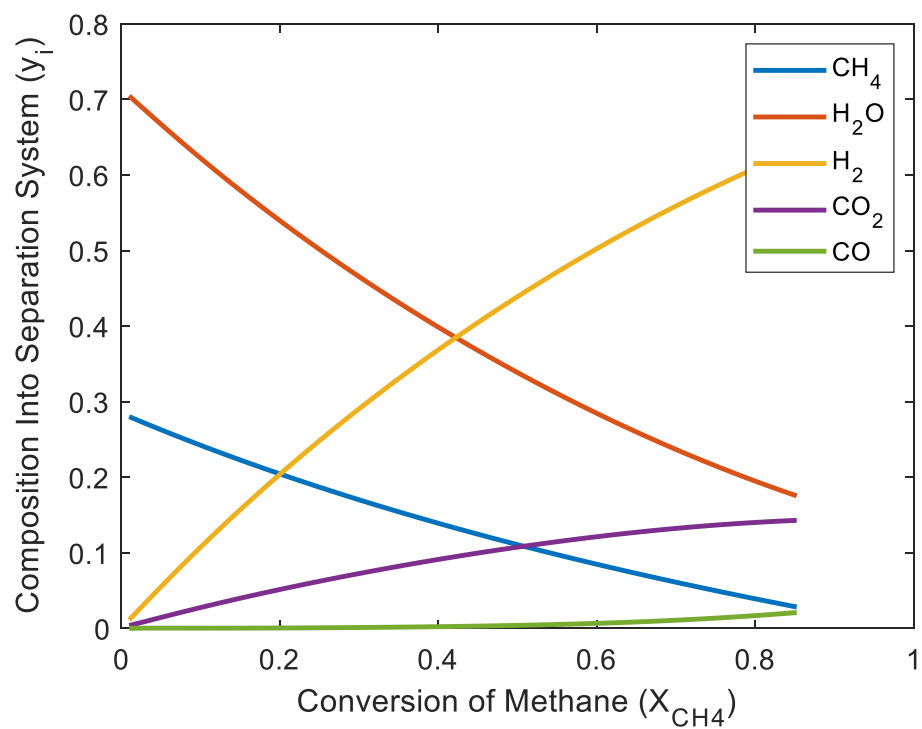




**Figure D.5** Production of all components in reactor 1 versus conversion of  $CH_4$



**Figure D.6** Component production rates of reactor 2 versus conversion of  $CH_4$



**Figure D.7** Composition of stream entering separation system versus conversion of  $CH_4$

## Appendix E: Distribution Modeling and Costing

### Assumptions - gaseous hydrogen tube trailer transportation

<b>Compression</b>	
P1	30 bar
P2	250 bar
P3	700 bar
F12	1982 mol/s
F23	57 mol/s
T1	303 K
T2	298 K
Number of first compressors	20
First Compressor BHP	980 hp
Secondary Compressor BHP	226 hp
<b>Delivery</b>	
Total truck capacity	300 kg H <sub>2</sub>
Pick up/drop-off time	2 hr/trip
Two-way drive distance	124 mi/trip
Tube trailer cost	\$150,000
Undercarriage Cost	\$60,000
Cab Cost	\$90,000
<b>Trucks</b>	
Truck Fuel Efficiency	6 mpg
Average speed	50 mi/hr
Driver Hours	8 hr/driver/day
load/unload time	2 hr/trip
truck availability	24 hr/day
truck availability	1 shifts/day
Driver Labor cost	28.75 \$/hr
Fuel Price	3 \$/gal
Truck lifetime	5 years

## Calculations

total trips	$\frac{63 * 10^6 kg}{yr} * \frac{trip}{300kg}$	210,000 trips/yr
miles traveled	$\frac{124 mi}{trip} * \frac{210,000 trips}{yr}$	26,040,000 mi/yr
travel time	$\frac{124 mi}{trip} * \frac{hr}{50 mi}$	2.48 hr/trip
total driving time	$\frac{2.48 hr}{trip} * \frac{210,000 trips}{yr}$	520,800 hr/yr
total time for loading/unloading	$\frac{2 hr}{trip} * \frac{210,000 trips}{yr}$	420,000 hr/yr
total delivery time	520,800 + 420,000 hr/yr	940,800 hr/yr
number of trucks needed	$\frac{210,000 trips}{yr} * \frac{truck day}{1 trip} * \frac{yr}{365 days} * \frac{12 plant yrs}{5 truck yrs}$	1,381 trucks
number of drivers needed	$\frac{940,800 hr}{yr} * \frac{day}{12 driver hrs} * \frac{yr}{365 days}$	215
Fuel needed	$\frac{26,040,000 mi}{yr} * \frac{gal}{6 mi}$	4,340,000 gal/yr

### Fixed Costs

tube trailer cost	\$207,123,288
undercarriage cost	\$82,849,315
truck cab cost	\$124,273,973
First compressor IC	\$53,825,229
35 Secondary compressors IC	\$28,235,453

### Variable Costs

H2 product cost (\$1670/MT)	\$105,178,500 /yr
labor costs	\$27,048,000 /yr
fuel costs	\$13,020,000 /yr
cost to power first compressors	\$6,141,255 /yr
cost to power 2nd compressors	\$2,472,924 /yr
O&M/AGS (fraction of revenue)	10%
*O&M	\$40,868,100 /yr
*AGS	\$40,868,100 /yr

### Profit

Price of H2 at pump	\$6.49 /kg
total H2 sold	63,000,000 kg/yr
Product Revenue	\$408,681,000 /yr

[illegible]

Taxable Earnings [MM\$]	Taxes Paid [MM\$]	After Tax Profit [MM\$]	Cash Flow [MM\$]	DF	DCF Discounted Cash Flow [MM\$]	NPV [MM\$]	NPV%	Pre-tax ROI [%]
0	0	0	0	1.00	0	0		
147	40	133	114	0.91	103	103	20.81%	34.87%
147	40	133	114	0.83	94	197	19.86%	34.87%
147	40	133	114	0.75	85	282	18.97%	34.87%
147	40	133	114	0.68	78	360	18.14%	34.87%
147	40	133	114	0.62	71	431	17.35%	34.87%
147	40	133	114	0.56	64	495	16.61%	34.87%
147	40	133	114	0.51	58	553	15.92%	34.87%
147	40	133	114	0.47	53	606	15.26%	34.87%
147	40	133	114	0.42	48	654	14.64%	34.87%
147	40	133	-383	0.39	-148	507	10.21%	34.87%
147	40	133	133	0.35	47	553	10.14%	34.87%
147	40	133	133	0.32	43	596	<b>10.00%</b>	34.87%

## Appendix F: MATLAB Code

**\*\* This function will take a desired conversion in reactor 1 ( $X_1$ ), conversion in reactor 2 ( $X_2$ ),  $T_1$ ,  $T_2$ ,  $P$ , and  $MR$ , and output all reactor sizes, an estimate for installation costs, energy costs, and automatically adjusts feed rate so 63 kta of hydrogen is always produced. Performs NPV analysis on the results based on correlations for equipment sizes and other costs. Also, will stop increasing reactor volume once a maximum conversion is reached.**

```
function
[X1,X2,Reactor1Comp,Reactor2Comp,Vtot1,Vtot2,Reactor1Prod,Reactor2Prod,FT_1,F
T_2,NPV,NPVP] = PlantSim(X_1,X_2,T1,T2,P,MR,dW,H2Price)
R1 = 8.314*10^(-3); %R constant for reaction kinetics
format shortEng
format compact
%% Information from Hysys
A1 = 649.3; %Area of each heat exchanger
%% Begin capacity loop
Capacity2 = 1;
err = 1;
iter = 0;
F1 = 1000;
while err > 0.001
    %% Flowrates into first reactor
    F1 = F1/Capacity2; %Flow rate of methane feed (mol/s)
    F2 = F1*MR; %Inlet feed of H2O (mol/s)
    W1 = 0; %Initial catalyst weight in reactor 1 (kg)
    W2 = 0; %Initial catalyst weight in reactor 2 (kg)
    FCH4 = 0.9963*F1; %molar flow of CH4
    FCO2 = 0.0037*F1; %molar flow of CO2
    FH2 = 0; %molar flow of H2
    FCO = 0; %molar flow of CO
    FH2O = F2; %molar flow of H2O
    %% Define flow stream into Reactor 1
    FCH4_1 = FCH4;
    FH2O_1 = FH2O;
    FH2_1 = FH2;
    FCO_1 = FCO;
    FCO2_1 = FCO2;
    FT_1 = FCH4 + FH2O + FH2 + FCO2 + FCO;
    MdotCH41 = (FCH4*16.04 + FH2*2.016 + FCO2*44.01 + FCO*28)*3600/1000;
    MdotH2O1 = (FH2O*18.01)*3600/1000;
    MdotRlin = (FCH4*16.04 + FH2*2.016 + FCO2*44.01 + FCO*28 +
    FH2O*18.01)*3600/1000;
    w0CH4 = FCH4*16.04/MdotRlin*3600/1000;
    w0H2O = FH2O*18.01/MdotRlin*3600/1000;
    w0H2 = FH2*2.016/MdotRlin*3600/1000;
    w0CO2 = FCO2*44.01/MdotRlin*3600/1000;
    w0CO = FCO*28/MdotRlin*3600/1000;
    %% Perform finite difference method to solve Reactor 1
    X1 = 0;
    while X1 < X_1
        FT = FCH4_1 + FH2O + FH2 + FCO2 + FCO; % Recalculate total molar flow
        PCH4 = (FCH4/FT)*P; %Recalculate all partial pressures
        PCO = (FCO/FT)*P;
        PH2O = (FH2O/FT)*P;
```



```

    PH2 = (FH2/FT)*P;
    PCO2 = (FCO2/FT)*P;
    k1 = k_1(T1,R1); %Calculate rate constants at each point in reactor 1
    k2 = k_2(T1,R1);
    k3 = k_3(T1,R1);
    K1 = K_1(T1);
    K2 = K_2(T1);
    KCO = K_CO(T1,R1); %Calculate equilibrium constants at each point in
reactor 1
    KH2 = K_H2(T1,R1);
    KCH4 = K_CH4(T1,R1);
    KH2O = K_H2O(T1,R1);
    PSI = PSI_(KCO,KH2,KCH4,KH2O,PCO,PH2,PCH4,PH2O);
    r1 = r_1(PSI,k1,K1,PH2,PCH4,PH2O,PCO); %Reaction rates at each point in
reactor 1
    r2 = r_2(PSI,k2,K2,PH2,PCO2,PH2O,PCO);
    r3 = r_3(PSI,k3,K1,K2,PCH4,PH2,PCO2,PH2O);
    FCH4 = FCH4 - r1*dW - r3*dW; %Change in all component molar flow rates
    FH2O = FH2O - r1*dW - r2*dW - 2*r3*dW;
    FCO = FCO + r1*dW - r2*dW;
    FCO2 = FCO2 + r2*dW + r3*dW;
    FH2 = FH2 + 3*r1*dW + r2*dW + 4*r3*dW;
    X1 = (FCH4_1-FCH4)/(FCH4_1); %Define conversion of methane at each
reactor size
    if W1 > 300000
        X_1 = X1;
        break
    end
    W1 = W1 + dW;
end
%% Set up initial conditions flowing into reactor 2
FCH4_2 = FCH4;
FH2O_2 = FH2O;
FH2_2 = FH2;
FCO2_2 = FCO2;
FCO_2 = FCO;
Reactor1Prod = [FCH4_2 FH2O_2 FH2_2 FCO2_2 FCO_2];
FT_2 = FCO_2 + FH2_2 + FCO2_2 + FH2O_2 + FCH4_2;
y1CH4 = FCH4_2/FT_2;
y1H2O = FH2O_2/FT_2;
y1H2 = FH2_2/FT_2;
y1CO2 = FCO2_2/FT_2;
y1CO = FCO_2/FT_2;
Reactor1Comp = [y1CH4 y1H2O y1H2 y1CO2 y1CO];
MdotR1out = (FCH4*16.04 + FH2*2.016 + FCO2*44.01 + FCO*28 +
FH2O*18.01)*3600/1000;
w1CH4 = FCH4*16.04/MdotR1out*3600/1000;
w1H2O = FH2O*18.01/MdotR1out*3600/1000;
w1H2 = FH2*2.016/MdotR1out*3600/1000;
w1CO2 = FCO2*44.01/MdotR1out*3600/1000;
w1CO = FCO*28/MdotR1out*3600/1000;
%% Solve Reactor 2 with finite difference
X2 = 0;
while X2 < X_2
    FT = FCH4 + FH2O + FH2 + FCO2 + FCO; % Recalculate total molar flow
    PCO = (FCO/FT)*P; %Recalculate all partial pressures
    PCO2 = (FCO2/FT)*P;
    PH2O = (FH2O/FT)*P;

```

```

PH2 = (FH2/FT)*P;
k4 = k_4(T2); %Calculate rate constants at each point in reactor 2
K2 = K_2(T2);
r4 = r_4(k4,K2,PCO,PH2O,PH2,PCO2); %Reaction rate in reactor 2
FH2O = FH2O - r4*dW; %Recalculate molar flow rates
FCO = FCO - r4*dW;
FCO2 = FCO2 + r4*dW;
FH2 = FH2 + r4*dW;
X2 = (FCO_2-FCO)/(FCO_2); %Define conversion of Carbon Monoxide
if W2 > 300000
    X_2 = X2;
    break
end
W2 = W2 + dW; %Add catalyst weight in each iteration
end
MdotR2out = (FCH4*16.04 + FH2*2.016 + FCO2*44.01 + FCO*28 +
FH2O*18.01)*3600/1000;
w2CH4 = FCH4*16.04/MdotR2out*3600/1000;
w2H2O = FH2O*18.01/MdotR2out*3600/1000;
w2H2 = FH2*2.016/MdotR2out*3600/1000;
w2CO2 = FCO2*44.01/MdotR2out*3600/1000;
w2CO = FCO*28/MdotR2out*3600/1000;
FCH4_3 = FCH4;
FH2O_3 = FH2O;
FH2_3 = FH2;
FCO2_3 = FCO2;
FCO_3 = FCO;
Reactor2Prod = [FCH4_3 FH2O_3 FH2_3 FCO2_3 FCO_3];
FT_3 = FCO_3 + FH2_3 + FCO2_3 + FH2O_3 + FCH4_3;
y2CH4 = FCH4_3/FT_3;
y2H2O = FH2O_3/FT_3;
y2H2 = FH2_3/FT_3;
y2CO2 = FCO2_3/FT_3;
y2CO = FCO_3/FT_3;
Reactor2Comp = [y2CH4 y2H2O y2H2 y2CO2 y2CO];
FH2O_out = FH2O;
FH2O = 0;
MdotComp = (FCH4*16.04 + FH2*2.016 + FCO2*44.01 + FCO*28 +
FH2O*18.01)*3600/1000;
wcompCH4 = FCH4*16.04/MdotComp*3600/1000;
wcompH2O = FH2O*18.01/MdotComp*3600/1000;
wcompH2 = FH2*2.016/MdotComp*3600/1000;
wcompCO2 = FCO2*44.01/MdotComp*3600/1000;
wcompCO = FCO*28/MdotComp*3600/1000;
FT_4 = FH2 + FCH4 + FCO2 + FCO; %Molar flow rate into compressor/PSA (mol/s)

%% Solve for size/mass of PSA
Phigh = 30*.987; %High PSA Pressure (atm)
Plow = 2*.987; %Low PSA Pressure (atm)
PCOhigh = Phigh*FCO/FT_4; %Partial pressure of CO into PSA (atm)
PColow = Plow*FCO/(FT_4-0.9*FH2); %Partial pressure of CO into PSA (atm)
T = 303; %Temp into PSA
fL = 0.95; %fraction of bed saturation
% Parameters for CO
k1 = 5.05;
k2 = -0.00905;
k3 = 0.001137;
k4 = 1617.0;

```

```

k5 = 0.5245;
k6 = 256.5;
n = k5 + k6/T;
B = k3*exp(k4/T);
qm = k1 + k2/T;
qH = (qm*B*PCOhigh^n)/(1+(B*PCOhigh^n));
qL = (qm*B*PCOlow^n)/(1+(B*PCOlow^n));
Mbed = (FCO)*300/((qH - qL)*fL); %mass of 1 PSA bed
VPSA = Mbed/795/.8; %volume of 1 PSA vessel (m^3)
LPSA = (VPSA*64/pi)^(1/3);
DPSA = .25*LPSA;
ProductH2 = 0.9*FH2; %Hydrogen production rate (mol/s)
Exhaust = FCO2; %All CO2 goes into exhaust
FH2_out = 0.1*FH2;
FCO_out = FCO;
FCH4_out = FCH4;
Capacity = ProductH2/1033.399; %Fraction of desired H2 product
err = abs(Capacity-1);
Capacity2 = Capacity;
iter = iter + 1;
end
%% Energy Balances for Costing
Reactor1W = 1000*(-241.83*(FH2O_2 - FH2O_1) - 393.51*(FCO2_2 - FCO2_1)...
    - 110.53*(FCO_2 - FCO_1) - 74.87*(FCH4_2 - FCH4_1)); %Energy to heat
reactor 1 (W)
Reactor2W = -1000*(-241.83*(FH2O_3 - FH2O_2) - 393.51*(FCO2_3 - FCO2_2)...
    - 110.53*(FCO_3 - FCO_2) - 74.87*(FCH4_3 - FCH4_2)); %Energy to cool
reactor 1 (W)
PreHeaterW = (T1 - 298)*(35.69*FCH4_1 + 43.7934*FCO2_1 + 29.24*FH2_1);
%Energy to heat methane feed to T1 (W)
BoilerW = 40700*FH2O_1 + 75.6*(212.5-80.7)*FH2O_1 + (380 -
212.5)*36.5*FH2O_1; %Energy to boil water in feed to steam at 380 Deg C (W)
ThermalW = BoilerW + PreHeaterW + Reactor1W;
FlashDrumW = (219-100)*(36.5*FH2O_3 + 35.69*FCH4_3 + 43.7934*FCO2_3 +
29.24*FH2_3 + 29.15*FCO_3) + 40700*FH2O_3; %Energy to cool stream and
condense water (W)
CompressorBHP = (3.3*10^(-5)/.254)*P*14.5038*(FT_4*8.314*10^(-
5)*373/P)*60*35.3147*((30/P)^.254 - 1)/.85; %BHP of compressor before PSA
CoolingWaterGJ = (FlashDrumW + Reactor2W)*3600*24*350/(10^9); %GJ of cooling
water per year (GJ/year)
PumpW = 50150/1107.8*F2; %Pump duty (W)
%% Reactor Sizing Parameters
pcat = 1000; %Bulk density of catalyst (kg/m^3)
Vtot1 = W1/pcat; %Total Reactor 1 volume (m^3)
Vtot2 = W2/pcat;%Total Reactor 2 volume (m^3)
L1 = (Vtot1*20^2/pi)^(1/3); %Reactor 1 length (m) (assumes 10:1 aspect ratio)
Dr1 = .1*L1; %Reactor 1 Diameter (m) (assumes 10:1 aspect ratio)
L2 = (Vtot2*20^2/pi)^(1/3); %Reactor 2 length (m) (assumes 10:1 aspect ratio)
Dr2 = .1*L2; %Reactor 2 Diameter (m) (assumes 10:1 aspect ratio)
%% Variable Costs
H2Energy = 1000*286*FH2_out; %Energy released by burning excess H2 (W)
COEnergy = 1000*294*FCO_out; %Energy released by burning excess CO (W)
CH4Energy = 1000*890*FCH4_out; %Energy released by burning excess CH4 (W)
EffluentW = H2Energy + COEnergy + CH4Energy; %Total energy from burning all
effluent (W)
EffluentCO2 = FCO_out + FCH4_out; %Total CO2 from burning all effluent
(mol/s)

```

```

EnergyRatio = ThermalW/EffluentW; %Decides if more methane is needed for
furnaces
if EnergyRatio < 1
    FurnaceCO2 = EnergyRatio*EffluentCO2;
    ThermalCost = 0; % Cost of thermal energy for furnaces ($/year)
else
    MethaneBurned = (ThermalW - EffluentW)/890000; %Total Methane burned in
furnaces (mol/s) (discounts energy from burned effluent)
    FurnaceCO2 = MethaneBurned + EffluentCO2; %CO2 Produced by furnaces
(mol/s)
    ThermalCost = (ThermalW - EffluentW)/1000000*10*24*350; % Cost of thermal
energy for furnaces ($/year)
end
TotalElectricityW = CompressorBHP*745.7 + PumpW; %Total Electricity Usage (W)
ElectricityCO2 = 1.512*10^(-12)*TotalElectricityW; %CO2 Produced from Elec.
(mol/s)
ElectricityCO2Cost = 8.8*10^(-3)*ElectricityCO2*3600*24*350; %Additional CO2
Cost from heaters ($/year)
FurnaceCO2Cost = 8.8*10^(-3)*FurnaceCO2*3600*24*350; %Additional CO2 Cost
from heaters ($/year)
CO2Cost = 4.4*10^(-3)*Exhaust*3600*24*350 + FurnaceCO2Cost +
ElectricityCO2Cost; %Total cost of sequestration ($/year)
FeedCost = .001879*F1*3600*24*350; %Cost of Methane Feed ($/year)
SteamFeedCost = .05*18.01/1000000*F2*3600*24*350; %Cost of Water Feed @ $0.05
per MT ($/year)
H2Revenue = H2Price/1000000*2.016*ProductH2*3600*24*350; %Income for H2
($/year)
CoolingWaterCost = CoolingWaterGJ*2; %Cost of all cooling water ($/year)
CompressorElectricity = CompressorBHP*745.7/1000000*50*24*350; %Electricity
powering compressor 1 ($/year)
PumpElectricity = PumpW/1000000*50*24*350; %Water pump electricity cost
WasteWaterCost = FH2O_out*3600*24*350*18.01/1000000*1.25; %Wastewater
treatment cost ($/year)
AllCosts = [ThermalCost WasteWaterCost CO2Cost FeedCost SteamFeedCost
CoolingWaterCost CompressorElectricity PumpElectricity]; %Vector of all
variable costs
%% Fixed Costs
Fp = 1;
Fm = 1;
Fc = Fm*Fp;
PreHeaterBTU = PreHeaterW*3.412/1000000;
Reactor1BTU = Reactor1W*3.412/1000000;
BoilerBTU = BoilerW*3.412/1000000;
Reactor1IC = (1650/280)*(101.9*((Dr1*3.28)^1.066)*((L1*3.28)^.82))*(2.18+Fc);
Reactor2IC = (1650/280)*(101.9*((Dr2*3.28)^1.066)*((L2*3.28)^.82))*(2.18+Fc);
FeedFurnaceIC = (1650/280)*(5.52*10^3)*(PreHeaterBTU^0.85)*(1.27+Fc); % Pre-
Reactor Furnace Installed Cost
BoilerIC = (1650/280)*(5.52*10^3)*(BoilerBTU^0.85)*(1.27+Fc);
Reactor1FurnaceIC = (1650/280)*(5.52*10^3)*(Reactor1BTU^0.85)*(1.27+Fc); %
Reactor Furnace Installed Cost
CompressorIC = (1650/280)*517.5*CompressorBHP^.82*(2.11+Fc); %Installed cost
of compressor 1
PSAIC = 4*(1650/280)*101.9*(DPSA*3.28)^1.066*(LPSA*3.28)^0.82*(3.18 + Fc) +
5*4*Mbed; %IC of 4 PSA tanks
HeatExchangerIC = (1650/280)*101.3*A1^.65*(2.29+Fc);
HeatExchangersIC = 16*HeatExchangerIC;
CatalystCost = (W1+W2)*30*3;

```

```

AllIC = [PSAIC Reactor1IC Reactor2IC FeedFurnaceIC BoilerIC Reactor1FurnaceIC
CompressorIC HeatExchangersIC]; %Vector of all Installation Costs ($)
%% NPV Calculations
ISBL = sum(AllIC); %Total installation cost ($)
PR = H2Revenue; %AARON - annual product revenue ($/yr)
VC = sum(AllCosts); %AARON - annual cost of feedstock ($/yr)
FC = ISBL;
PBT = H2Revenue - sum(AllCosts);

Sigma = 6.8137;
a = 4.1107;
b = -0.3498;
c = 0.2936;
d = -2.06;
e = 3.4057;
f = 7.011;
g = 1.177;
h = 1.214;
k = 12;

TCI = h*FC;
ROIbt = PBT/TCI;
NPV = a*PBT+b*FC;
NPVP = c*ROIbt+d;

end

%% Functions for finding kinetic parameters
function k1 = k_1(T,R)
    k1 = 0.04*2.763*10^(-6)*exp((-240.1/R)*(1/T - 1/648));
end
function k2 = k_2(T,R)
    k2 = 0.04*.11337*exp((-67.13/R)*(1/T - 1/648));
end
function k3 = k_3(T,R)
    k3 = 0.04*3.289*10^(-7)*exp((-243.9/R)*(1/T - 1/648));
end
function k4 = k_4(T)
    k4 = 3.33*10^(-8)*exp(12.88-1855.5/T);
end
function K1 = K_1(T)
    K1 = exp(-26830/T + 30.114);
end
function K2 = K_2(T)
    K2 = exp(4400/T - 4.036);
end
function KCO = K_CO(T,R)
    KCO = 40.91*exp((70.65/R)*(1/T - 1/648));
end
function KH2 = K_H2(T,R)
    KH2 = 0.0296*exp((82.9/R)*(1/T - 1/648));
end
function KCH4 = K_CH4(T,R)
    KCH4 = 0.1791*exp((38.28/R)*(1/T - 1/823));
end
function KH2O = K_H2O(T,R)
    KH2O = 0.4152*exp((-88.68/R)*(1/T - 1/823));

```

```

end
function PSI = PSI_(KCO,KH2,KCH4,KH2O,PCO,PH2,PCH4,PH2O)
    PSI = 1 + KCO*PCO + KH2*PH2 + KCH4*PCH4 + (KH2O*PH2O/(PH2+.01));
end
function r1 = r_1(PSI,k1,K1,PH2,PCH4,PH2O,PCO)
    r1 = (k1/((PH2+.01)^2.5 * PSI^2))*(PCH4*PH2O - (PH2^3 * PCO/K1));
end
function r2 = r_2(PSI,k2,K2,PH2,PCO2,PH2O,PCO)
    r2 = (k2/((PH2+.01)*PSI^2))*(PCO*PH2O - (PH2*PCO2/K2));
end
function r3 = r_3(PSI,k3,K1,K2,PCH4,PH2,PCO2,PH2O)
    r3 = (k3/((PH2+.01)^3.5*PSI^2))*(PCH4*PH2O^2 - (PH2^4*PCO2/(K1*K2)));
end
function r4 = r_4(k4,K2,PCO,PH2O,PH2,PCO2)
    r4 = k4*PCO*PH2O*(1-(PH2*PCO2/(K2*PCO*PH2O)));
end

```

**\*\* This script is used in conjunction with the function above to form the plots required for the report**

```

clear;
clc;
close all

```

```

Price = 1300;

```

```

NPVPmax1 = -Inf;
NPVPmax2 = -Inf;

```

```

T1 = 873:20:1273;
T2 = 473:20:773;

```

```

for i = 1:length(T1)
    [X11(i),~,~,~,~,~,~,~,~,~,NPV1(i),NPVP1(i)] =
    PlantSim(1,1,T1(i),773,20,2.5,0.3,Price);

```

```

    if NPVP1(i) > NPVPmax1
        NPVPmax1 = NPVP1(i);
    end
end

```

```

for i = 1:length(T1)
    [X12(i),~,~,~,~,~,~,~,~,~,NPV2(i),NPVP2(i)] =
    PlantSim(1,1,T1(i),773,15,2.5,0.3,Price);

```

```

    if NPVP2(i) > NPVPmax1
        NPVPmax1 = NPVP2(i);
    end
end

```

```

for i = 1:length(T1)

```

```

[X13(i),~,~,~,~,~,~,~,~,~,NPV3(i),NPVP3(i)] =
PlantSim(1,1,T1(i),773,10,2.5,0.3,Price);

    if NPVP3(i) > NPVPmax1
        NPVPmax1 = NPVP3(i);
    end
end

for i = 1:length(T2)
    [X14(i),~,~,~,~,~,~,~,~,~,NPV4(i),NPVP4(i)] =
PlantSim(1,1,1153,T2(i),20,2.5,0.3,Price);

    if NPVP4(i) > NPVPmax2
        NPVPmax2 = NPVP4(i);
    end
end

for i = 1:length(T2)
    [X15(i),~,~,~,~,~,~,~,~,~,NPV5(i),NPVP5(i)] =
PlantSim(1,1,1153,T2(i),15,2.5,0.3,Price);

    if NPVP5(i) > NPVPmax2
        NPVPmax2 = NPVP5(i);
    end
end

for i = 1:length(T2)
    [X16(i),~,~,~,~,~,~,~,~,~,NPV6(i),NPVP6(i)] =
PlantSim(1,1,1153,T2(i),10,2.5,0.3,Price);

    if NPVP6(i) > NPVPmax2
        NPVPmax2 = NPVP6(i);
    end
end

MaxLine1 = NPVPmax1*ones(length(T1));
MaxLine2 = NPVPmax2*ones(length(T2));

figure('DefaultAxesFontSize',12)
plot(NPV1/1000000,NPVP1,'LineWidth',2)
hold on
plot(NPV2/1000000,NPVP2,'LineWidth',2)
hold on
plot(NPV3/1000000,NPVP3,'LineWidth',2)
hold on
plot(NPV4/1000000,NPVP4,'LineWidth',2)
hold on
plot(NPV5/1000000,NPVP5,'LineWidth',2)
hold on
plot(NPV6/1000000,NPVP6,'LineWidth',2)
legend('P = 20 bar','P = 15 bar','P = 10 bar')
xlabel('NPV_p_r_o_j, $MM')

```

```

ylabel('NPV_%')
xlim([-85 -20])

figure('DefaultAxesFontSize',12)
plot(T1-273,NPVP1,'LineWidth',2)
hold on
plot(T1-273,NPVP2,'LineWidth',2)
hold on
plot(T1-273,NPVP3,'LineWidth',2)
hold on
plot(T1-273,MaxLine1,'g--','LineWidth',2)
legend('P = 20 bar','P = 15 bar','P = 10 bar','Max NPV_%')
xlabel('Reactor 1 Temperature (Deg C)')
ylabel('NPV_%')

figure('DefaultAxesFontSize',12)
plot(T2-273,NPVP4,'LineWidth',2)
hold on
plot(T2-273,NPVP5,'LineWidth',2)
hold on
plot(T2-273,NPVP6,'LineWidth',2)
hold on
plot(T2-273,MaxLine2,'g--','LineWidth',2)
legend('P = 20 bar','P = 15 bar','P = 10 bar','Max NPV_%')
xlabel('Reactor 2 Temperature (Deg C)')
ylabel('NPV_%')

clear;
clc;
close all

Price = 1300;

NPVPmax1 = -Inf;
NPVPmax2 = -Inf;

X_1 = 0.01:0.01:0.99;
X_2 = 0.01:0.01:0.99;

for i = 1:length(X_1)
    [X11(i),~,~,~,~,~,~,~,~,NPV1(i),NPVP1(i)] =
    PlantSim(X_1(i),1,1153,573,20,2.5,0.3,Price);
    [X12(i),~,~,~,~,~,~,~,~,NPV2(i),NPVP2(i)] =
    PlantSim(X_1(i),1,1153,573,20,3.0,0.3,Price);
    [X13(i),~,~,~,~,~,~,~,~,NPV3(i),NPVP3(i)] =
    PlantSim(X_1(i),1,1153,573,20,3.5,0.3,Price);

    if NPVP1(i) > NPVPmax1
        NPVPmax1 = NPVP1(i);
    end
    if NPVP2(i) > NPVPmax1
        NPVPmax1 = NPVP2(i);
    end
    if NPVP3(i) > NPVPmax1
        NPVPmax1 = NPVP3(i);
    end
end

```



```

end
end

for i = 1:length(X_2)
    [~,X21(i),~,~,~,~,~,~,~,NPV4(i),NPVP4(i)] =
    PlantSim(1,X_2(i),1153,573,20,2.5,0.3,Price);
    [~,X22(i),~,~,~,~,~,~,~,NPV5(i),NPVP5(i)] =
    PlantSim(1,X_2(i),1153,573,20,3.0,0.3,Price);
    [~,X33(i),~,~,~,~,~,~,~,NPV6(i),NPVP6(i)] =
    PlantSim(1,X_2(i),1153,573,20,3.5,0.3,Price);
    if NPVP4(i) > NPVPmax2
        NPVPmax2 = NPVP4(i);
    end
    if NPVP5(i) > NPVPmax2
        NPVPmax2 = NPVP5(i);
    end
    if NPVP6(i) > NPVPmax2
        NPVPmax2 = NPVP6(i);
    end
end

MaxLine1 = NPVPmax1*ones(length(X_1));
MaxLine2 = NPVPmax2*ones(length(X_2));

figure('DefaultAxesFontSize',12)
plot(X11,NPVP1,'LineWidth',2)
hold on
plot(X12,NPVP2,'LineWidth',2)
hold on
plot(X13,NPVP3,'LineWidth',2)
hold on
plot(X_1,MaxLine1,'g--','LineWidth',2)
legend('MR = 2.5','MR = 3.0','MR = 3.5','Max NPV_%')
xlabel('Reactor 1 Conversion (X_C_H_4)')
ylabel('NPV_%')

figure('DefaultAxesFontSize',12)
plot(X21,NPVP4,'LineWidth',2)
hold on
plot(X22,NPVP5,'LineWidth',2)
hold on
plot(X33,NPVP6,'LineWidth',2)
hold on
plot(X_2,MaxLine2,'g--','LineWidth',2)
legend('MR = 2.5','MR = 3.0','MR = 3.5','Max NPV_%')
xlabel('Reactor 2 Conversion (X_C_O)')
ylabel('NPV_%')

clear;
clc;
close all;

Price = 1300;
dW = 0.3;

```

```

X_1 = 0.01:0.01:0.99;
X_2 = X_1;
P = 20;

for i = 1:length(X_1)

[X1(i),X2(i),Reactor1Comp(i,:),Reactor2Comp(i,:),Vtot1(i),Vtot2(i),Reactor1Pr
od(i,:),Reactor2Prod(i,:),FT_1(i),FT_2(i),NPV(i),NPVP(i)] =
PlantSim(X_1(i),1,1153,573,P,2.5,dW,Price);
end

figure('DefaultAxesFontSize',12)
plot(X1,Reactor1Comp(:,1),X1,Reactor1Comp(:,2),X1,Reactor1Comp(:,3),X1,Reacto
r1Comp(:,4),X1,Reactor1Comp(:,5),'LineWidth',2)
xlabel('Conversion of Methane (X_C_H_4)')
ylabel('Composition Leaving Reactor 1 (y_i)')
legend('CH_4','H_2O','H_2','CO_2','CO')

figure('DefaultAxesFontSize',12)
plot(X1,Vtot1,'LineWidth',2)
xlabel('Conversion of Methane (X_C_H_4)')
ylabel('Reactor 1 Volume (m^3)')

figure('DefaultAxesFontSize',12)
plot(X1,Reactor1Prod(:,1),X1,Reactor1Prod(:,2),X1,Reactor1Prod(:,3),X1,Reacto
r1Prod(:,4),X1,Reactor1Prod(:,5),'LineWidth',2)
xlabel('Conversion of Methane (X_C_H_4)')
ylabel('Production of Reactor 1 (F_i) (mol/s)')
legend('CH_4','H_2O','H_2','CO_2','CO')

figure('DefaultAxesFontSize',12)
plot(X1,FT_1,'LineWidth',2)
xlabel('Conversion of Methane (X_C_H_4)')
ylabel('Flowrate into Reactor 1 (mol/s)')

figure('DefaultAxesFontSize',12)
plot(X1,Reactor2Comp(:,1),X1,Reactor2Comp(:,2),X1,Reactor2Comp(:,3),X1,Reacto
r2Comp(:,4),X1,Reactor2Comp(:,5),'LineWidth',2)
xlabel('Conversion of Methane (X_C_H_4)')
ylabel('Composition Into Separation System (y_i)')
legend('CH_4','H_2O','H_2','CO_2','CO')

for i = 1:length(X_2)

[X1(i),X2(i),Reactor1Comp(i,:),Reactor2Comp(i,:),Vtot1(i),Vtot2(i),Reactor1Pr
od(i,:),Reactor2Prod(i,:),FT_1(i),FT_2(i),NPV(i),NPVP(i)] =
PlantSim(1,X_2(i),1153,573,P,2.5,dW,Price);
end

figure('DefaultAxesFontSize',12)
plot(X2,Reactor2Comp(:,1),X2,Reactor2Comp(:,2),X2,Reactor2Comp(:,3),X2,Reacto
r2Comp(:,4),X2,Reactor2Comp(:,5),'LineWidth',2)
xlabel('Conversion of Carbon Monoxide (X_C_O)')
ylabel('Composition Leaving Reactor 2 (y_i)')
legend('CH_4','H_2O','H_2','CO_2','CO')

```

```

figure('DefaultAxesFontSize',12)
plot(X2,Vtot2,'LineWidth',2)
xlabel('Conversion of Carbon Monoxide (X_C_O)')
ylabel('Reactor 2 Volume (m^3)')

figure('DefaultAxesFontSize',12)
plot(X2,Reactor2Prod(:,1),X2,Reactor2Prod(:,2),X2,Reactor2Prod(:,3),X2,Reactor2Prod(:,4),X2,Reactor2Prod(:,5),'LineWidth',2)
xlabel('Conversion of Methane (X_C_H_4)')
ylabel('Production of Reactor 2 (F_i) (mol/s)')
legend('CH_4','H_2O','H_2','CO_2','CO')

figure('DefaultAxesFontSize',12)
plot(X2,FT_2,'LineWidth',2)
xlabel('Conversion of Carbon Monoxide (X_C_O)')
ylabel('Flowrate into Reactor 2 (mol/s)')

```

**\*\* The following script was used to iterate through all possible design variables for optimum NPV%**

```

clear;
clc;
close all
dW = 0.3;
Price = 1300;
T1 = 953:20:1273;
T2 = 473:20:773;
X_1 = 0.1:0.01:0.99;
X_2 = 0.1:0.01:0.99;
P = 5:0.5:20;
MR = 2.5:0.1:5;
NPVmax = -Inf;
for i = 1:length(T1)

[X1,X2,Reactor1Comp,Reactor2Comp,Vtot1,Vtot2,Reactor1Prod,Reactor2Prod,FT_1,F
T_2,NPV,NPVP] = PlantSim(1,1,T1(i),773,20,2.5,dW,Price);
    if NPV >= NPVmax
        OptT1 = T1(i);
        NPVmax = NPV;
    end
end
for i = 1:length(T2)

[X1,X2,Reactor1Comp,Reactor2Comp,Vtot1,Vtot2,Reactor1Prod,Reactor2Prod,FT_1,F
T_2,NPV,NPVP] = PlantSim(1,1,OptT1,T2(i),20,2.5,dW,Price);
    if NPV >= NPVmax
        OptT2 = T2(i);
        NPVmax = NPV;
    end
end
for i = 1:length(P)

[X1,X2,Reactor1Comp,Reactor2Comp,Vtot1,Vtot2,Reactor1Prod,Reactor2Prod,FT_1,F
T_2,NPV,NPVP] = PlantSim(1,1,OptT1,OptT2,P(i),2.5,dW,Price);
    if NPV >= NPVmax
        OptP = P(i);
    end
end

```

```

        NPVmax = NPV;
    end
end
for i = 1:length(MR)

[X1,X2,Reactor1Comp,Reactor2Comp,Vtot1,Vtot2,Reactor1Prod,Reactor2Prod,FT_1,F
T_2,NPV,NPVP] = PlantSim(1,1,OptT1,OptT2,OptP,MR(i),dW,Price);
    if NPV >= NPVmax
        OptMR = MR(i);
        NPVmax = NPV;
    end
end
for i = 1:length(X_1)

[X1,X2,Reactor1Comp,Reactor2Comp,Vtot1,Vtot2,Reactor1Prod,Reactor2Prod,FT_1,F
T_2,NPV,NPVP] = PlantSim(X_1(i),1,OptT1,OptT2,OptP,OptMR,dW,Price);
    if NPV >= NPVmax
        OptX1 = X1;
        NPVmax = NPV;
    end
end
for i = 1:length(X_2)

[X1,X2,Reactor1Comp,Reactor2Comp,Vtot1,Vtot2,Reactor1Prod,Reactor2Prod,FT_1,F
T_2,NPV,NPVP] = PlantSim(OptX1,X_2(i),OptT1,OptT2,OptP,OptMR,dW,Price);
    if NPV >= NPVmax
        OptX2 = X2;
        NPVmax = NPV;
    end
end
end

```