\Solar-thermal Conversion of Biomass to Methanol in the United States Southwest

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Table of Contents

Figures

Tables

I. Executive Summary

Objectives

The purpose of this project is to design and analyze the economic feasibility of a methanol production facility that is powered by solar-thermal energy. Our solar process has an advantage over other technologies in that it does not produce tar byproducts, which are costly to remove in non-solar-thermal processes. The project's objective is an annual production of 56 million gallons of fuel grade methanol. Seventy acres of 4000 concentrated sun heliostats with a secondary radiation recovery mirror will provide an estimated 553GW-hr annually to the solar reactor.

The economic feasibility was analyzed over a 16 year period, which includes one year for plant construction. Total permanent investment (TPI) of capital into the project is approximately $294 MM with a working capital requirement of $31.582 MM. In order to achieve a 12.5% investor's rate of return (IRR) the selling price of methanol is calculated to be $1.56/gal. Returns on investment (ROI) and corresponding payback period are 15.4% and 6.5 years respectively. The net present value (NPV) at the end of each year is $203.022 MM. Given a market price of $1.33/gallon (1), the process is not economically viable given the current problem specifications.

Recommendations

Given the current problem specifications the plant should not be built. However, the use of a longer plant lifetime, raising equity via an issue of stock in the parent company, and increased government subsidies will affect the economic feasibility and should be investigated.

II. Project Description and Scope

The aim of this project is to design a facility that will produce 56 million gallons of 99.97% pure methanol per year from readily available biomass feed stock and methane in the south-western United States. In order to accomplish these goals, Aspen HYSYS™ and Aspen Plus™ were used to model and simulate the process. Economic analysis of the process includes an estimation of total capital investment, target methanol selling price, and sensitivity analysis.

III. Background Information

Need for Renewable Fungible Fuels

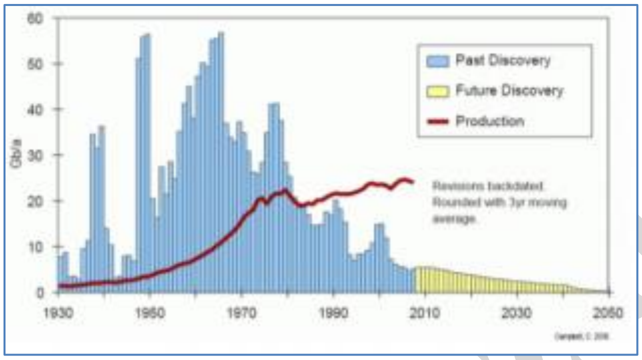
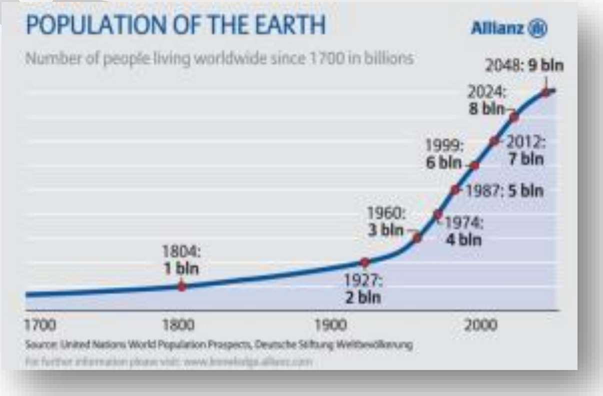


Figure 1 Conventional Oil: Discoveries vs. Production

The world is running out of oil. According to the chart at right (2) oil discovery peaked in the 1960's and has been falling ever since. On December 7, 2010, OPEC announced that it is cutting production of its current reserves by 70,000 barrels per day (3). Compounding this problem is the fact that since the advent of the atom bomb and other modern technology, world population has ceased to be linear and has begun to grow exponentially (4).

Estimates suggest that between 2007 and 2035, total world energy consumption will increase by roughly 49% (5). As the dominant superpower, the United States uses a disproportionately large amount of oil in comparison to its population size, accounting for roughly 25% of total world consumption of energy in comparison to being home to roughly 5% of the world's population. As the Chinese and Indian economies continue to grow, they place greater pressure on the world stocks, driving the price of energy up, and increasing the rate that we are diminishing our stocks (6). As a strategic resource, the United States needs to develop alternative and supplemental energy resources to fuel its current levels of consumption.



Source: United Nations World Population Prospects, Deutsche Stiftung Weltbevölkerung

Figure 2 Worldwide Population since the 18th Century

As an alternative to oil, other types of energy must be explored. “Fungible fuels” offer the same or better energy content as today’s hydrocarbons and can easily be incorporated into the existing fuel distribution infrastructure. To be fungible, a fuel should offer the same or better energy content as today’s hydrocarbons, and should use the same distribution pipelines, tankers and other assets. As the world transitions to these new sources, these renewable fuels will eliminate the distribution constraints on biofuels, enabling producers to rapidly scale up operations.

Biofuels have some significant advantages over other types of renewable energy such as wind or solar, the most notable being the current infrastructure in the United States. While both are clean options, neither has as large of a potential benefit as biofuel processes do, and also have issues with energy storage that have yet to be solved. Other possible technologies have been researched such as splitting water to produce hydrogen as an energy carrier. In order to use hydrogen gas as a fuel for transportation, massive changes and construction are needed to supply fuel for domestic consumption. Biofuels are a potential alternative to gasoline and diesel. They have similar compositions to traditional petroleum derived fuels, and are widely available throughout the United States.

Currently there are two pathways for producing biofuels: via biological organisms or through thermo-chemical production. While production of biofuels via the biochemical pathway using algae or other organisms has the advantage of minimizing carbon emissions, these processes have some disadvantages. Biochemical reactions are relatively slow compared to their thermo-chemical counter parts, largely due to their sensitive temperature constraints, resulting in significantly larger plants and reactors. Algae, yeast, and other viable producers have the disadvantage of synthesizing unwanted byproducts, resulting in large downstream separations and lower yields.

In contrast to the limitations that a biochemical pathway presents, a thermo-chemical pathway allows for the synthesis of many different target molecules and requires far less energy in purifying the products downstream. High temperature (> 1200 °C) thermal cracking of biomass has the potential to produce high yields of synthesis gas while avoiding side reactions which produce tar and other unwanted chemicals. By utilizing existing synthesis gas technology and high temperature solar technology, the project develops a process that is sustainable, clean, and potentially economically viable.

Biomass Gasification

Traditionally the gasification of biomass has been used to produce methanol and other products using coal as a feedstock. However, as demand for energy continues to rise other sources of fuel which were once not permissible for economic reasons are now being investigated. Biomass is an excellent candidate for conversion into methanol due to its high energy density and availability.

The composition of the feed used in this project is given in Table 1.

Table 1 Biomass Feed Composition

Component	Wt%
Cellulose	68.25
Lignin	21.75
Ash	8.78
N	0.61
S	.01
Cl^-	.06

The conversion of biomass to methanol begins with gasification of the feed stock inside of a solar reactor. Methane gas and water combine with the biomass to produce synthetic gas (syngas). The biomass feed is primarily composed of cellulose and lignin, the products of which are shown in reactions 1 and 2 respectively. Sulfur, nitrogen, and chlorine are also present in significant quantities, and the products of these are given in Equations 3, 4, and 5 respectively.

$$C_6H_{10}O_5 + 6H_2O \rightarrow 6CO + 6H_2 \qquad (1)$$

$$C_{10}H_{12}O_3 + 7H_2O \rightarrow 10CO + 13H_2 \qquad (2)$$

$$S + H_2 \rightarrow H_2S \qquad (3)$$

$$2N \rightarrow N_2 \qquad (4)$$

$$2Cl + H_2 \rightarrow 2HCl \qquad (5)$$

The addition of methane gas increases the yield as this is a highly exothermic reaction which helps to lower the free energy barrier of the gasification reactions by coupling the gasification of biomass inside of the solar reactor. In this first step 100% conversion is achieved. The products of the gasification of methane are given in Equation 6.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (6)$$

As the syngas begins to cool after leaving the solar reactor, the products experience an abrupt change and react with water in what is known as the water gas shift reaction (WGS). During production this quenching step is accomplished by addition of water into the vapor stream where it reaches equilibrium as shown in Equation 7.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (7)$$

Before the syngas can continue to be processed, the ash waste of the gasification reaction needs to be removed as well as other contaminants that poison catalysts located inside the methanol reactor. In particular, the sulfur and chlorine need to be removed in order to meet product specifications and environmental regulations. The hydrogen sulfide and hydrogen chloride gas are removed via the reaction with zinc oxide catalyst in a gas cleaning bed as shown in Equations 8 and 9. Also, these species are highly corrosive and it is optimal to remove them as quickly as possible as the product is a harmless water vapor.

$$ZnO_{(s)} + H_2S \rightarrow ZnS_{(s)} + H_2O \qquad (8)$$

$$ZnO_{(s)} + 2HCl \rightarrow ZnCl_{2(s)} + H_2O \qquad (9)$$

The vapor is then combined with a recycle stream and compressed in order to feed into the methanol reactor. Many studies indicate that maximum conversion of CO occurs over a $CuO/ZnO/Al_2O_3/ZrO_2$ catalyst via the hydrogenation of the carbon species during the competing reverse water shift reaction. Many different carbon species are produced in this step; however, for the purposes of this study it is assumed that methanol synthesis occurs via the reactions given in Equations 10, 11, and 12 with a total conversion in each reaction of 45%.

$$CO + 2H_2 \rightarrow CH_3OH \qquad (10)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (11)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (12)$$

The mechanism by which this step occurs has been extensively studied, however, there is still much disagreement in the literature as to the way in which the catalyst facilitates the reaction. Therefore, for simplification purposes, the calculations performed in this study assume no adsorption and that the volumetric flow rate of the gas mixture only varies with the change in the identities of the various component species that occur during the course of reaction.

As the world increases demand for fuels such as methanol, larger plants are being built to meet the demand. The following figure corresponds to a fixed-bed reactor designed by Lurgi MegaMethanol of Frankfurt, Germany, and is designed to produce up to 5000 MTPD[1] of methanol.

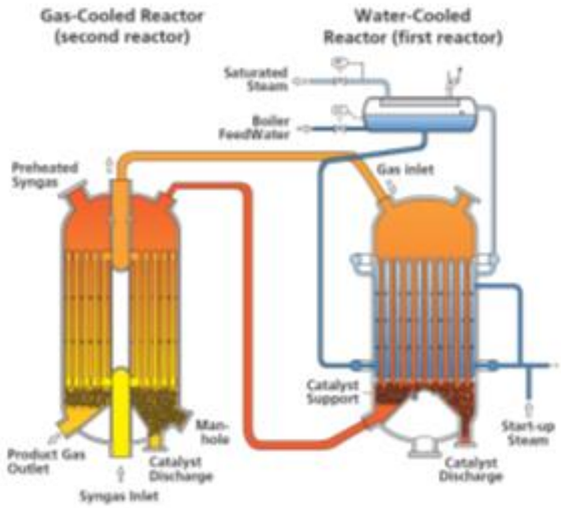


Figure 3 Lurgi MegaMethanol Reactor

Solar Energy

Solar energy to power various processes has been increasingly used in recent years due to its environmentally friendly mode of operation and thermodynamic advantages (7). The sun is an ideal choice as an immediate source of energy as it is readily available across the face of the earth and a renewable source of energy. Given that if only one-tenth of one percent of the non-inhabited land space on earth was covered with solar collectors at a mere twenty percent efficiency, we could gather enough energy to meet the world's yearly energy needs. The possibility of attaining a sustainable source of energy, free of geopolitical conflict, is within our reach since the solar energy reserve is virtually unlimited (7).

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[1] MTPD stands for metric tonnes per day

Although solar energy continues to be a promising source of power, there remain a few drawbacks which are currently hampering the wide-spread development of solar dependent processes. The first has to do with the natural limitations of the earth and sun. Solar radiation is intermittent, dilute, and unequally distributed over the surface of the earth, which makes it difficult to depend on completely. A solution for this problem is to convert solar energy into chemical energy carriers. The second drawback is the cost associated with developing solar thermochemical processes and implementing them; but as researchers continue to perfect the technology and demand increases for solar equipment, this should not be a problem in the long run.

Solar Thermochemical Processing

Capturing and using the sun's energy has proved to be exceedingly difficult. However, given the advancements in technology that have occurred at break neck speed over the past decade, scientists and engineers have begun to develop processes that exploit these advances in an effort to produce products that meet the needs of an ever increasingly demanding public. A solar thermochemical process is defined as an "endothermic process that uses concentrated solar energy as the source of high-temperature process heat" (7). One such process that utilizes solar energy is the gasification of biomass for the production of methanol.

A solar reactor is used to power the gasification of biomass for the production of syngas that is then used to synthesize the methanol product. There are three different optical configurations for large-scale collection and concentration of solar energy as seen in figure below: (A) the trough system, (B) the tower system, and (C) the dish system.

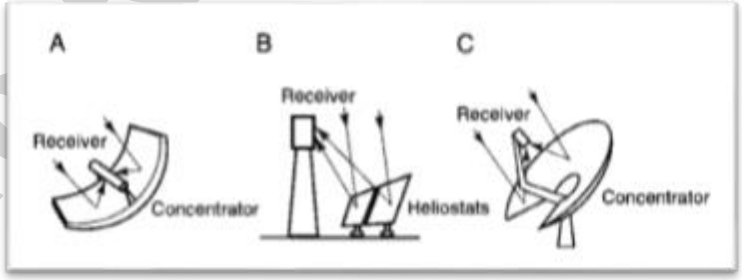

Figure 4 Central Receiver Optical Configurations[2]

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[2] Figure from p. 624, Encyclopedia of Energy, Volume 5. ©

In this study, a central receiver tower system is used to provide energy to the reactor due to its ability to generate a great deal of power at high temperatures with a reasonable efficiency according to Mr. Allan Lewandowski, an expert heliostat field designer.[3] The process utilizes a central receiver field design. The heliostat field is primarily composed of heliostat mirrors, arranged in a series in order to reflect light from the sun towards a specified target. The radiation from the sun is then used to heat up a central receiver that brings enough energy for the reaction to take place. A model configuration of heliostats is given in the following figure for a single receiver.[4]

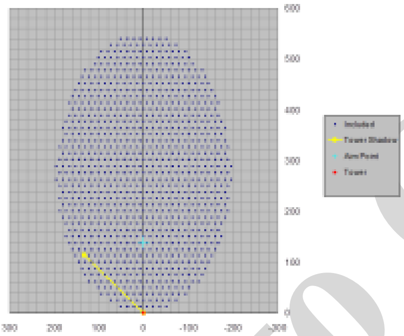

Figure 5 Heliostat configuration for a single field

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[3] The information contained herein is taken from a presentation given to the Chemical and Biological Engineering Senior Process Design Class in November 2010

[4] The source of the figure is a PowerPoint™ presentation given by Mr. Allan Lewandowski. The heliostat field parameters are $q_c = 35^o$, $g = 35^o$, C = 3.0, Heliostat Area = 93400 m^2

IV. Safety, Environmental and Health Considerations

Recent tragedies remind us how safety concerns are imperative to plant personnel, local communities, and the environment. According to the philosopher George Santayana, "Those who forget history are doomed to repeat it." For example: safety guidelines that were neglected resulted in catastrophic consequences following the accidents in Texas City, Bhopal, and more recently in the Gulf of Mexico. The best way to avert similar disasters is to regiment safety systems and guidelines that prevent accidents and outline emergency procedures in the un-likely event of an accident. In addition, routine checks must be implemented to make sure key safety systems and guidelines are properly working and being followed.

Figure 6 BP™ refinery in Texas City after the explosion

Personnel Safety

As witnessed in 2005's Texas City Refinery explosion, production of hydrocarbon fuels poses significant dangers to plant personnel. The Explosion in Texas City killed 15 and injured over 170 individuals. Keeping these catastrophic events in mind, preventing similar safety risks at this plant must be the highest priority. The first line of defense against disaster is having a code of safety that is paramount over anything else. In order to facilitate a code of safety, all plant employees must submit to extensive pre-employment training and routine refresher courses on safety issues. Continuous education on safety policy will result in a team that is not only aware of safety risks but also knowledgeable about how to detect such risks and how to act in an emergency.

Once on the job, all plant personnel will be required to wear personal protective equipment (PPE) including: steel toed boots, a hard hat, protective clothing, and safety glasses. In addition to the prior pieces of PPE, operators working close to noisy equipment will be required to wear ear plugs. Proper HAZMAT equipment will be available to personnel in event of any emergency. Gear such as respirators and proper protective clothing will be available to operators required to do routine cleaning and inspection of unit operations dealing with corrosives. The entire plant will also be well ventilated with appropriate HVAC units to ensure that workers are not exposed to hazardous materials.

To ensure personnel safety remains at a high level throughout the year, random inspections will be conducted on a monthly basis. Random drills will also be conducted which will test personnel in different safety scenarios ranging from small chemical spills to full scale disasters.

Community Safety

In terms of human cost, the chemical spill at Bhopal, India is the worst industrial disaster in history. Though sources range in mortality estimates, most agree that approximately 15,000 people died quickly due to the massive exposure to methyl isocyanate (MIC). This estimate does not include the thousands that died or suffered from long term health effects due to moderate exposure to MIC in outlying plant areas. Bhopal is a city of roughly 1.4 million people which was in the immediate vicinity of the Union Carbide plant producing vinyl chloride which reflects poor planning and negligence on behalf of the Union Carbide executives and engineering staff (8).

Daggett is a small city of roughly 560 located near the intersection of I-40 and I-15 in the southwestern California desert. By picking a far less populated area than Bhopal, the plant minimizes the potential danger of building a methanol plant in a well-populated area. Just as plant personnel needs to be aware of all safety concerns, the community also needs to be aware of the possible dangers associated with producing methanol in this process. Safety programs for the community will provide them with necessary information needed in the event of an accident or any kind of exposure. Safety planning and regular drills will be organized with local authorities to ensure an immediate and appropriate response should any type of accident or safety hazard occur.

Figure 7 Fires Burning and oil covering the surface of the water around the BP oil

Environmental Concerns

While some may debate the validity of climate change, none can deny that the world is running out of easily refined energy resources (9). The solar-thermal gasification plant contributes towards an independence from petroleum by using biomass as its raw material rather than crude oil. In addition to displacing petroleum, using solar power to run the primary solar reactor will not only cut down on utilities, but will also eliminate carbon emissions that would be generated in a coal-fired power plant.

Consequently, this produces chemical energy for cars and transportation while maintaining a low carbon footprint.

Shortcuts in safety implementation by management involved in the 2010 BP oil spill led to what is estimated to be the most massive man-made oil spill in history. Yet to come are the full long-term effects of this disaster. So far, the public has seen significant biological destruction of marine life, as well as a large blow to the Gulf Costal region economy which relies on fishing. To avoid another disaster like the BP oil spill, safety systems must be implemented thoroughly throughout the plant. Real time temperature, pressure, and flow rate measuring at every step of the process will ensure process stability. In addition to key process monitoring, a system will be implemented to continually test the integrity and accuracy of key instruments used to monitor the process. Physical process integrity examinations will be performed by the normal operators on a daily basis. More elaborate examinations will be performed on a routine schedule by trained inspectors. Safety system implementation and key daily inspection will ensure the long term success of the project from a safety perspective.

Hazardous and corrosive materials are produced as side products during this process, most notably hydrogen sulfide and hydrogen chloride. Both species are reacted with Zinc Oxide in the following reactions.

$ZnO + H_2S \rightarrow ZnS\ (s) + H_2O$ (100% conversion of H_2S)

$ZnO + 2HCl \rightarrow ZnCL_2\ (s) + H_2O$ (100% conversion of HCl)

These hazardous species are removed to prevent damage to downstream components and to reduce the risk of exposure to hazardous materials. Zinc Sulfide (10) and Zinc Chloride (11) are skin permeable and pose health risks to plant personnel but are far easier to contain and properly dispose than their unreacted counterparts. All local, state, and federal permits and guidelines will be strictly followed in order to further protect the environment from any potential contamination. The most important goal during production is to ensure the safety of all plant personnel, the environment, and the community at large. Any risks to safety will be considered a breach of the plant's safety code and will be taken seriously in order to reach an appropriate solution.

Material Considerations

Component	Biomass (Cellulose)	Carbon Dioxide	Carbon Monoxide	Hydrogen	Hydrogen Chloride	Hydrogen Sulfide	Methane
Health Risks	Irritant on contact, causes GI problems if ingested	Asphyxiant, Powerful Vasodialator	Replaces Oxygen	Replaces Oxygen	Highly Corrosive	Highly Corrosive	Replaces Oxygen
Reactivity	none	Some metals, hydrides, cesium monoxide, sodium peroxide mixed with aluminum/ magnesium	Oxidizers, halogens, metal oxides and lithium	oxidizers	Aluminum, copper, stainless steel, oxidizers, alkalis, water	Nitric acid, oxidizers, chlorine.	oxidizers, halogens and oxygen
Fire/Explosive data	Combustible at high temp. May explode if powdered	no fire/non explosive	Flammable	high fire / high explosive	Non-Flammable	Flammable	high fire / high explosive
Phase	solid	gas	gas	gas	liquid	gas	gas
Boiling Point C	Decomposes	-78.5	-191.5	-252.8	110	-60.28	-161.6
Melting Point C	500	-56.5	-205	-259.2	-27.32	-82.3	-182.5
Density g/cm^3	1.5	1.977 g/L@1 atm and 0 C	1.25 g/L @ 1 atm and 0 C	.0899 g/L	1.18	1.363 g/L	416 kg/m^3
Appearance	fibrous and off-white	invisible	invisible	invisible	light yellow	light yellow	invisible
MW (g/mol)	NA	44.01	28.01	2.016	36.46	34.082	16.42
Formula	$C_6H_{10}O_5$	CO_2	CO	H_2	HCl	HS	CH_4

Methanol	Nitrogen	Water	Zinc Chloride	Zinc Oxide	Zinc Sulfate
toxic, inhibits CNS quickly	Replaces Oxygen	none	Irritant / toxic	Irritant / toxic	Irritant / toxic
oxidizers, reducers, alkali metals, Acid chlorides, powdered aluminum and magnesium	none	alkali metals, HS	oxidizers, metals, cyanides, sulphides	HCL, H2S, Magnesium, Absorbs CO_2	Oxidizers, Iodine pentachloride
high fire / high explosive	none	none	none	none	none
liquid	gas	liquid	solid	solid	solid
64.7	-195.79	99.98	756	2360	Na
-97	-210	0	292	1975	1185
0.7918		1	2.907	5.606	4.09
clear	invisible	clear	white	white	white
32.04	28.2	18.015	136.315	81.408	97.474
CH_3OH	N_2	H_2O	ZnCl	ZnO	ZnS

Unit operations Considerations

Operation	Concern	Safety Precautions
Cutter	Rotating blades pose a risk to operators	Machinery sealed during operation. Guards installed Restricted Access
Grinder	Rotating drum can open, and send projectiles large distances Risk to operators due to moving parts	Guards installed Hard hats required on plant grounds Restricted Access
Heliostat	High temperature Extremely High Radiative flux	Minimum distance during operation Eye protection required for close proximity work
Tower	Physical height	Fall prevention equipment (ropes, harnesses, etc.)
Solar Reactor	High temperature Extremely High Radiative flux	Minimum distance during operation Eye protection required for close proximity work
Quench Tank	High Temperature Dry Drowning	Minimum distance during operation. Cleaning procedures in place (SCBA, etc.)
Cyclone	Extreme Temperatures Dust (risk to lungs)	Guards installed Minimum safe distance during operation Masks required during operation
Fixed-Bed Reactor	Catalyst removal ZnO dust Corrosive components	Use argon gas to cool reactor before changing out catalyst Masks required Appropriate PPE required Special training for HCl and acids
Multi-Stage Compressor	Moving parts pose a risk to operatos	Guards installed
Methanol Reactor	High Pressure High Temperature Exothermic Reaction	Restricted Access In case of runaway reaction install argon cooling stream and emergency shutoff valves
Flash Drum	High Pressure	Restricted Access
Storage Tank	Large volume of combustible material Liquid overflow	Install appropriate fire equipment Install tee and valve to divert liquid flow away to secondary containment
Distillation Tower	Extreme temperatures Combustible materials Physical height Column flooding	Guards installed Minimum safe distance during operation Fall prevention equipment (ropes, harnesses, etc.) Install liquid level gauges and emergency shutoff valves
Flares	Open flame	Guards installed

V. Project Premises

Plant Design

- Target of 56 million gallons off methanol per year
- Methanol must be 99.97% pure exiting the distillation tower
- Located in Daggett, California
- Upstream solar process runs 8 hours a day, 365 days a year
- Downstream process runs 24 hours a day totally 8000 hours a year
- Plant built from the ground up. No old plant used
- Gasification takes place in a reactor heated with solar-thermal energy provided by a heliostat field
- Biomass is fed to the reactor with the following compositions:
- Biomass is supplied as a liquid

Table 2 Biomass Composition and Properties

Component	Wt%	ΔH_c (J/g)
Cellulose	68.25	17340.76
Lignin	21.75	21178
Ash	8.78	
N	0.61	
S	.01	
Cl	.06	

- Methane is supplied as a gas via local pipelines
- Solar thermal reactor tubes made out of Silicon Carbide
- Solar thermal reactor operates at 35 bar and 1450 °C
- Flux into the solar reactor is ~ 500 kW/m^2
- In the solar reactor the following reactions occur:
    - $C_6H_{10}O_5$ (Cellulose) + $H_2O \rightarrow 6\ CO + 6\ H_2$ (100% conversion of cellulose)
    - $C_{10}H_{12}o_3$ (lignin) + $7\ H_2o \rightarrow 10\ CO + 13\ H_2$ (100% conversion of lignin)
    - $S + H_2 \rightarrow H_2S$ (100% conversion of S)
    - $2N \rightarrow 2N_2$ (100% conversion of N)
    - $2\ Cl + H_2 \rightarrow 2\ HCl$ (100% conversion of Cl^-)
    - $CH_4 + H_2O \rightarrow CO + 3\ H_2$ (100% conversion of CH_4)

- No higher weight tar is produced in the solar-thermal reactor
- There is a recycle stream fed from the end of the methanol reactor back to the solar-thermal reactor.
- Synthesis Gas undergoes an equilibrium reaction as it leaves the solar-thermal reactor:
  - $CO + H_2O \leftrightarrow CO_2 + H_2$
- This reaction happens at 800 °C and 35 bar
- Spray-Quench tank is modeled via:
  - Heat exchanger with an approach temp of 0.5 °C, and exit temp of 210 °C
  - Water is fed to the heat exchanger at 35 bar and 90 °F
  - The water and cooled gas streams are combined with a mixer
  - 0.5% of quench water ends up in process stream
- The ZnO reactor has the following reactions take place:
  - $ZnO\ (s) + H_2S \rightarrow ZnS\ (s) + H_2O$ (100% conversion of H_2S)
  - $ZnO\ (s) + 2HCl \rightarrow ZnCl_2\ (s) + H_2O$ (100% conversion of HCl)
- 100% of ZnS and $ZnCl_2$ are removed in splitter
- Methanol reactor is fed with Synthesis gat at 80 bar
- The following reactions and conversions take place in the methanol reactor:
  - $CO_2 + H_2 \rightarrow CO + H_2O$ (45% conversion of CO_2)
  - $CO + 2\ H_2 \rightarrow CH_3OH$ (45% conversion of CO)
  - $CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$ (45% conversion of CO_2)
- Methanol stream is decompressed to 35 bar and cooled to 50 °C
- The purge stream is flared and contains 0.5% of products leaving the separator
- The recycle stream contains 9.5% of the products leaving the separator
- All other material from the top of the separator is recycled to extinction

Economic Design

- Heliostats cost \$126/m^2 installed
- Secondary concentrator mirror costs \$1260/m^2 installed
- Base cost of the tower installed in terms of its height (m) is given by:
  - $\$[600{,}000 + 17.72 \times Height(m)^{2.392}] \times 1.41$
- Cost of natural gas is \$4/SCF
- Cost of biomass is \$60/metric ton delivered via rail
- 2.5 gallons of methanol are required to produce 1 gallon of gas
- An advanced biofuel credit of \$0.40 helps offset production costs
- High pressure steam at 450 psig costs \$17.29/1000 kg
- Medium pressure steam at 150 psig costs \$12.57/1000 kg
- Low pressure steam at 50 psig costs \$7.86/1000 kg
- Electricity costs \$0.06/kW-hr
- Cooling Water costs \$0.19/m^3
- Refrigeration at -150°F costs \$15/GJ
- Refrigeration at -90°F costs \$12.21/GJ
- Refrigeration at -30°F costs \$9.43/GJ
- Refrigeration at 10°F costs \$6.57/GJ
- Chilled water at 40°F costs \$4.71/GJ
- Wastewater treatment costs \$0.31/kg organic removed
- Landfill costs \$0.19/dry kg
- Low purity ZnO catalysts costs \$0.20/kg
- Silicon Carbide Tubes costs \$1,000/ft and has dimensions 6" OD and 3/4" thick
- Interest on capital is 4.5%
- Solar process runs 8 hr/day 365 days/yr
- Methanol process runs 24 hr/day 333 days/yr for a total of 8000 hr/yr
- Plant capacity starts at 50% in the first year of operation, increases to 75% in the second year of operation, and runs at full capacity beginning in the third year of operation
- Plant lifetime is 15 years
- Construction period is 1 year
- Contingency fund of 15%
- Inflation is assumed to be 1.9% /yr

- Effective tax rate of 38.9%
- Insurance and local taxes are 2%
- Total Fixed Cost is used in cash flow calculations[5]
- Cost of labor (annual wages per operator) is $104,000/operator/shift
- Royalties are $0.264/gal Methanol
- Methanol excise tax is $0.09/gal
- Depreciation of 7 year MACR
- 12.5% IRR

Figure 8 ATLAS MegaMethanol Plant

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[5] i.e. no depreciation of investment on fixed operating cost sheet

VI. Approach

Heats of Reaction for Lignin and Cellulose

The standard heat of reaction was calculated using Hess's Law, via the following equation as provided in Felder and Rousseau (2003):

$$\Delta\widehat{H}^{\circ}_{rxn} = \sum_{reactants} |\nu_i|\left(\Delta\widehat{H}^{\circ}_{c}\right)_i - \sum_{products} |\nu_i|\left(\Delta\widehat{H}^{\circ}_{c}\right)_i$$

Where ν_i is the stoichiometric coefficient of the reaction for species i, and ΔH_c is the heat of combustion for species i. From this equation we can calculate the heat of reaction for dry cellulose and lignin with steam at a standard 25 °C using the heats of combustion. The reactions for dry cellulose and lignin with steam are given as follows respectively.

$$C_6H_{10}O_{5(s)} + H_2O_{(g)} \longrightarrow 6CO_{(g)} + 6H_{2(g)}$$

$$C_{10}H_{12}O_{3(s)} + 7H_2O_{(g)} \longrightarrow 10CO_{(g)} + 13H_{2(g)}$$

The calculated values are summarized in Table 3 below.[6]

In order to calculate the heats of reaction at 1450 °C, the heat capacities were used to measure the change in the enthalpy of the reactants and products for the change in temperature. The heat capacities are provided for dry cellulose, lignin, and ash in the problem statement and are given as follows.

$$C_{p,cellulose} = \int (-0.01174 + 6.7207 \times 10^{-4}\, T)dt \ (\mathrm{kJ/mol\ K})$$

$$C_{p,lignin} = \int (0.03143 + 3.944 \times 10^{-4} T)dt \ (\mathrm{kJ/mol\ K})$$

$$C_{p,ash}(298K) = 705 \ (\mathrm{J/kg\ K})$$

The heat capacities of the additional chemical species methane and water are calculated using values from Table B.2 in Felder and Rousseau.[7] (12) In order to calculate the heats of reaction at the higher

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[6] For the full set of calculations consult Appendix A. Approach Calculations

[7] Heat capacities of the form: $C_{p,i} = a \times 10^3 + b \times 10^6 T + c \times 10^8 T^2 + d \times 10^{12} T^3$

temperature, we assumed a reference state of 1450 °C. The change in enthalpy required to cool the reactants in the feed to 25 °C is added to the heat of reaction at the same temperature. To this value is added the change in enthalpy required to heat the synthetic gas products in the effluent back up to a gasification temperature of 1450 °C. This approach is possible because the change in enthalpy of a chemical species with respect to a certain temperature is a state property.

The following equations are used to calculate the heat of reaction for cellulose and lignin respectively at a temperature of 1450 °C.

$$\Delta\hat{H}_{rxn,cellulose}(1450°C) = \int_{1723.15}^{298.15} C_{p,cellulose}\,dT + \int_{1450}^{100} C_{p,H_2O(g}\,dT + \Delta\hat{H}_{vap}(25°C) + \int_{100}^{25} C_{p,H_2O}\,dT + \Delta\widehat{H_r}(25°C) + 6\int_{25}^{1450} C_{p,CO}\,dT + 6\int_{25}^{1450} C_{p,H_2}\,dT$$

$$\Delta\hat{H}_{rxn,lignin}(1450°C) = \int_{1723.15}^{298.15} C_{p,lignin}dT + 7\int_{1450}^{100} C_{p,H_2O(g)}dT + 7\Delta\hat{H}_{vap}(25°C) + 7\int_{100}^{25} C_{p,H_2O(l)}dT + \Delta\widehat{H_r}(25°C) + 10\int_{25}^{1450} C_{p,CO}\,dT + 13\int_{25}^{1450} C_{p,H_2}dT$$ [8]

The following Table 3 summarizes the heats of reaction at a reference temperature of 25 °C and the operating temperature of the solar reaction of 1450 °C.

Table 3 Calculated Heats of Reaction

Species	$\Delta\hat{H}^{\circ}_{rxn}$ **(25 °C) (kJ/mol)**	$\Delta\hat{H}^{\circ}_{rxn}$ **(1450 °C) (kJ/mol)**[9]
Cellulose	601.47	89.51
Lignin	2729.33	2432.97

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[8] For detailed calculations consult Appendix A. Approach Calculations, Heats of Reaction

[9] The thermodynamic properties were all solved using EXCEL™

Biomass Feed Rate

Initially very simple mass and energy balance are carried out in order to familiarize ourselves with the process and in order to provide initial feed rates and the amount of energy that will be needed in the production of 56 million gallons per year of methanol. The feed composition is defined using the values provided in the problem statement. The initial biomass, methane, and steam feeds are then defined with respect to final annualized methanol production of 56 million gallons of 99.97% pure methanol using the given conversion profiles for each reaction step provided in the problem statement. For simplification purposes we assume 100% of the biomass is converted into synthetic gas at a temperature of 1450 °C, but quickly water-gas-shift equilibrium occurs as the solar reactor effluent stream begins to cool, which we assume occurs at 800 °C.

For the water-gas-shift (WGS) reaction, we can estimate the equilibrium constant using the following equation found in the literature (13).

$$K_{eq} = exp\left[-4.33 + \frac{4577.8}{T}\right]$$

The WGS reaction occurs at a temperature of 800 °C, which gives us an equilibrium constant, K_{eq}, equal to approximately 0.94. The equilibrium constant can also be expressed in terms of concentrations.[10]

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

Since the solar effluent stream lacks carbon dioxide, the extent (x) of the forward WGS reaction is equal to the amount of carbon dioxide produced in the WGS reactor. As a result, the equilibrium constant can also be represented by the following equation:

$$K_{eq} = \frac{[x]\left[H_{2,0} + x\right]}{[CO_0 - x][H_2O_0 - x]}$$

After the removal of ash, and hydrogen sulfide and hydrogen chloride has been accounted for via the reaction with ZnO, the reaction which results in methanol production is modeled for which we assume there is a 100% conversion of the carbon species to methanol. This is a very reasonable assumption for calculating the biomass and methanol feed rate required to input into this process since the unreacted

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[10] Where T is the temperature in K

carbon species are recycled through the methanol reactor to achieve a higher conversion. From this raw methanol production step virtually no carbon monoxide and carbon dioxide are escaping.

The total amount of methanol in mols/year the process needs to produce is calculated from the target annual production of 56 million gallons of 99.97% methanol using the properties of methanol given in the following Table 4. This gives us a value of 5.40E+09 mols/year.[11]

Table 4 Physical Properties of Methanol

Methanol Properties		
Density	0.7918	g/cm3
MW	32.04	g/mol

In order to solve for the initial biomass and methane feed rates, we set the H_2/CO molar flow rates of the WGS reaction to a target ratio of two as well as taking into account the previous assumptions made in this section, and use the solver function in EXCEL™ to give us the optimal biomass, methane, and steam feed rates summarized in Table 5.

Table 5 Optimal Solar Reactor Feed Rates

Feed	Feed Rate (kg/hr)
Biomass	26016.09
Methane	14029.59
Water	32428.80

Solar Reactor Energy Requirement

The theoretical energy requirement is calculated using the heats of reaction calculated in the previous section in addition to the heat of reaction of the methane with steam as given by the following equation.

$$CH_{4(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3H_{2(g)}$$

The equation for the heat of reaction of methane at the given temperature of 1450 °C is developed in a similar manner as outlined in the section on the heats of reaction of dry cellulose and lignin.

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[11] For detailed calculations consult Appendix A. Approach Calculations, Biomass Feed Rate Calculations

$$\Delta\widehat{H_r}(1450°C) = \int_{1450}^{100} C_{p,methane}dT + \int_{1450}^{100} C_{p,H_2O(g)}dT + \Delta\widehat{H}_{vap}(25°C) + \int_{100}^{25} C_{p,H_2O(l)}dT$$
$$+ \Delta\widehat{H_r}(25°C) + \int_{25}^{1450} C_{p,CO}dT + 3\int_{25}^{1450} C_{p,H_2}dT$$

Given the heat of reaction of methane, the amount of energy required to power the gasification of biomass and methane to produce high quality syngas can be calculated. This is accomplished by heating the reactants in the feed to the reaction temperature of 1450 °C and adding the heat of reaction for each species, then multiplying the resulting changes in enthalpy by the molar feed rates. For simplification purposes only the cellulose, lignin, ash, water, and methane are taken into consideration as seen in the following equation.[12]

$$E_{solar} = n_{cellulose}\left[\int_{298.15}^{1723.15} C_{p,cellulose}dT + \Delta\widehat{H}_{rxn,cellulose}(1450°C)\right]$$
$$+ n_{lignin}\left[\int_{298.15}^{1723.15} C_{p,lignin}dT + \Delta\widehat{H}_{rxn,lignin}(1450°C)\right] + n_{ash}\int_{1723.15}^{298.15} C_{p,ash}dT$$
$$+ n_{H_2O}\left[\int_{25}^{100} C_{p,H_2O(l)}dT + \Delta\widehat{H}_{vap,H_2O}(25°C) + \int_{100}^{1450} C_{p,H_2O(g)}dT\right]$$
$$+ n_{CH_4}\left[\int_{100}^{1450} C_{p,CH_4}dT + \Delta\widehat{H}_{rxn,CH_4}(1450°C)\right]$$

This gives a value of 189.27 MW required to power the process for the given molar flow rates, which results in a total of 552.66 GW-hr needed to power the process on an annual basis.[13]

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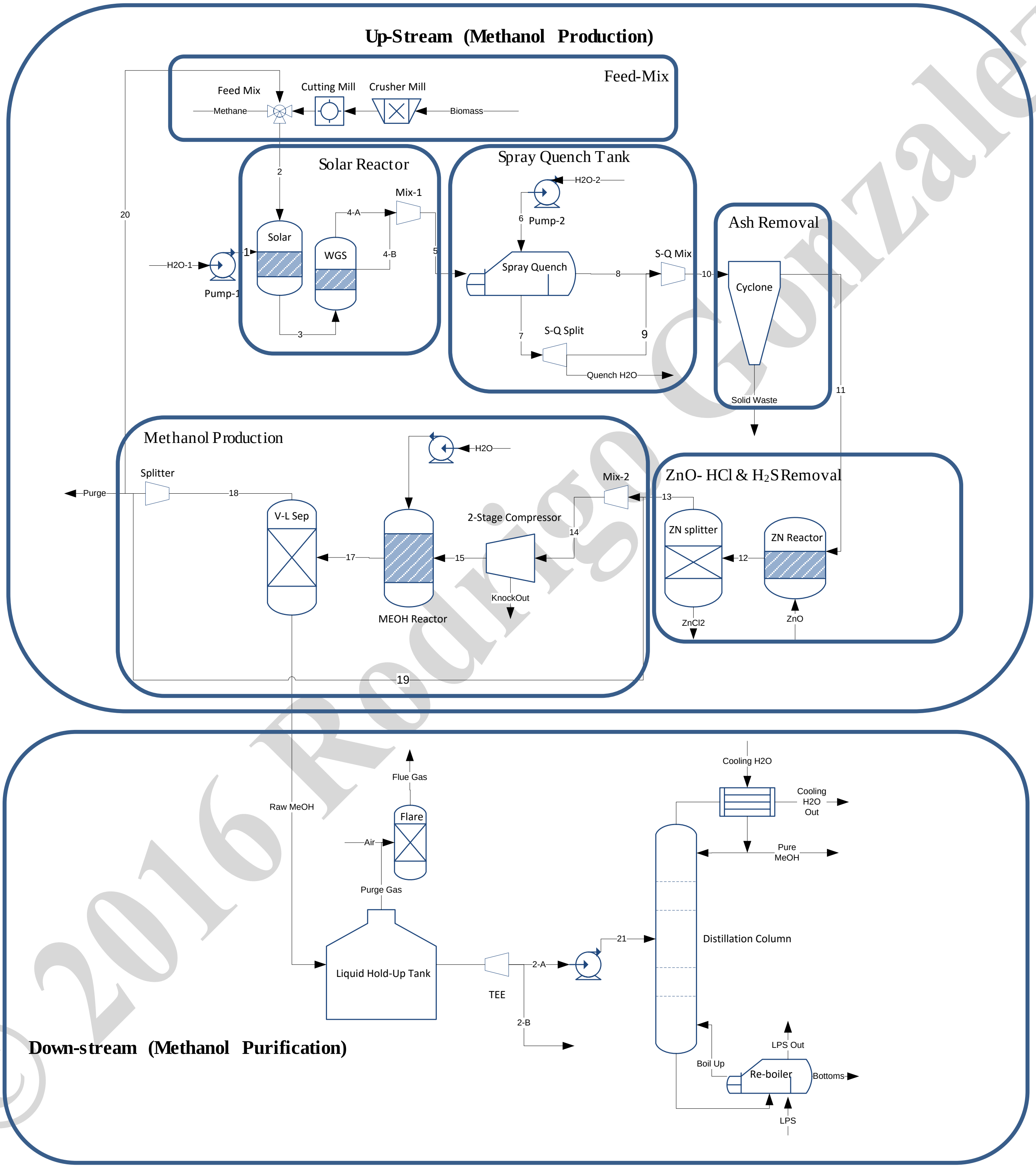
[12] For detailed calculations consult Appendix A. Approach Calculations, Theoretical Solar Reactor Energy Requirement Calculations

[13] Since the solar reactor can only run when sunlight is available (during the day) we assume the process runs an average of 8 hrs a day (2920 hrs a year)

VII. Process Flow with Material & Energy Balances

Process flow diagram for overall solar-thermal gasification process for producing methanol



Material and Energy Balances

Feed Mixing

Before biomass is fed to the solar reactor, it is chopped and grinded to an appropriate size for reacting with water and methane. Once chopped and grinded, the biomass is mixed with methane from a pipe-line and a recycle gas stream (20). Biomass is assumed to have the composition specified by the problem statement shown in the following table.

Table 6 Summary of Biomass Feed Composition

Component	Wt%
Cellulose	68.25
Lignin	21.75
Ash	8.78
N	0.61
Cl	0.01
S	0.60

The methane feed stream is assumed to be pure methane and the recycle gas stream is assumed to have the composition simulated by Aspen Plus™ shown in the following table.

Table 7 Summary of recycle gas stream

	Stream 20	
Component	Molar flow (kmol/sec)	Composition (mol%)
CO	0.05685981	0.220320107
H_2	0.18614515	0.721274295
N_2	0.01107093	0.042897584
CO_2	4.82E-05	0.000186831
methanol	0.00390136	0.01511697
water	5.27E-05	0.000204213
total	0.25807817	1

A summary of overall mass and energy flows related to the feed mixer are represented in Table 8.

Table 8 Summary of mass and energy flows into the feed mixer

Feed Mixer		
Stream	Mass Flow (kg/hr)	Enthalpy Flow (kJ/hr)
Biomass	317.3979	4.12E+06
Methane	14067.09	-6.53E+07
20	8662.058	-2.49E+07
2	23046.54	-1.91E+08

Solar Reactor:

Synthetic gas (syngas) is produced in the initial unit operation in the up-stream process. Although there are several unit operations used to model the solar reactor shown in Figure 10, there is actually only one reactor used in the production of syngas. Since solar-thermal technology is relatively new, simulation programs such as Aspen Plus™ used to simulate this process are not able to adequately model the process in one unit operation.

Operating at 35 bar and 1450°C, the solar reactor converts a mixture of water, biomass, and methane into syngas inside silicon carbide tubes. Two feeds enter the solar reactor including process water and a mixture of biomass, methane, and recycle gas (20) from the end of the up-stream process. Since biomass arrives in large bails by rail-car, the biomass is chopped and grinded which is then mixed with methane and the recycle gas before it is fed to the solar reactor. Process water fed into the solar reactor must be pumped to 35 bar and 298 K before it is fed to the reactor. The overall solar reactor process is diagramed in Figure 10.

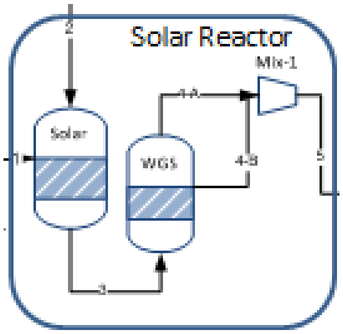


Figure 9 Diagram of overall solar reactor unit operation and individual operations used for its simulation

A summary of composition, material, and energy streams related to the overall solar reactor unit operation are shown in the following table.

Table 9 Summary of flows related to solar reactor

Solar Reactor							
	Stream	Component	Molar flow (kmol/sec)	Composition (mol%)	Overall Enthalpy Flow (kJ/hr)	T (K)	Pressure (bar)
In	2	CO	0.057	0.102	-2.77E+08	304.9	1.013
		H_2	0.186	0.335			
		S	0.000	0.000			
		N	0.003	0.006			
		N_2	0.011	0.020			
		Cl-	0.001	0.002			
		methane	0.244	0.438			
		CO_2	0.000	0.000			
		methanol	0.004	0.007			
		water	0.000	0.000			
		cellulose	0.030	0.055			
		lignin	0.009	0.016			
		ash	0.011	0.019			
		total	0.556	1.000			
	1	water	0.350	1.000	-3.60E+08	298	35
Out	5	CO	0.565	0.310	-1.24E+08	1073.15	35
		H_2	1.217	0.667			
		H_2S	0.000	0.000			
		N_2	0.013	0.007			
		HCl	0.001	0.001			
		CO_2	0.005	0.003			
		methanol	0.004	0.002			
		water	0.010	0.005			
		cellulose	0.000	0.000			
		lignin	0.000	0.000			
		ash	0.011	0.006			
		total	1.826	1.000			

After the components are fed to the reactor, they are assumed to go to complete conversion via the following stoichiometric equations:

$C_6H_{10}O_5$ (cellulose) + $H_2O \rightarrow 6\,CO + 6\,H_2$ (1)

$C_{10}H_{12}O_3$ (lignin) + $7\,H_2O \rightarrow 10\,CO + 13\,H_2$ (2)

$S + H_2 \rightarrow H_2S$ (3)

$2\,N \rightarrow N_2$ (4)

$2\,Cl^- + H_2 \rightarrow 2\,HCl$ (5)

$CH_4 + H_2O \rightarrow CO + 3\,H_2$ (6)

A summary of mass and energy balances for the solar reactor can be seen in Table 10.

Table 10 Summary of mass & energy balances for the solar reactor

Solar Reactor		
	In	Out
Mass Flow (kg/hr)	71444.48	71444.3
Enthalpy Flow (kJ/hr)	-6.38E+08	-1.24E+08
Heat Duty (kJ/hr)	5.13E+08	

Spray Quench Tank

The syngas produced in the solar reactor leaves in stream 5 at 1073.15K and 35 bar and is rapidly cooled to 210°C in the spray quench tank (Spray-Q). Typically, water is sprayed onto a hot vapor stream (5) where it is heated to its bubble point and removes heat from the hot process gas. In order to model this process via simulation software, a heat exchanger (SPRAY-Q) was employed. In the simulation, the heat exchanger was specified as countercurrent flow with a minimum temperature approach of 0.5°C. Also, since the syngas must be quenched to 210°C, the hot outlet temperature was specified as 210°. The Spray quench unit operation is diagramed in Figure 11.

The resulting water/syngas mixture leaving the actual spray quench tank is modeled by splitting the heated exit water stream (7) and then mixing it with the cold side exit stream (4). A summary of all spray quench streams are summarized in Table 11.

Table 11 Summary of material & energy streams related to spray quench unit operation

Spray Quench Tank							
	Stream	Component	Molar flow (kmol/sec)	Composition (mol%)	Overal Enthalpy Flow (kJ/hr)	T (K)	Pressure (bar)
In	5	CO	0.565	0.310	-1.24E+08	1073.15	35
		H_2	1.217	0.667			
		H_2S	0.000	0.000			
		N_2	0.013	0.007			
		HCl	0.001	0.001			
		CO_2	0.005	0.003			
		methanol	0.004	0.002			
		water	0.010	0.005			
		cellulose	0.000	0.000			
		lignin	0.000	0.000			
		ash	0.011	0.006			
		total	1.826	1.000			
	H2O-2	water	2.282	1	-2.34E+09	305.3722	35
Out	10	CO	0.56516452	0.308	-2.52E+08	483.15	35
		H_2	1.21712319	0.663			
		H_2S	2.25E-05	0.000			
		N_2	0.01264456	0.007			
		HCl	0.00122303	0.001			
		CO_2	0.00504911	0.003			
		methanol	0.00390136	0.002			
		water	0.02141736	0.012			
		cellulose	0	0.000			
		lignin	0	0.000			
		ash	0.01055992	0.006			
		total	1.837105588	1.000			
	Quench-H20	water	2.2706033	1	-2.21E+09	490.36	35

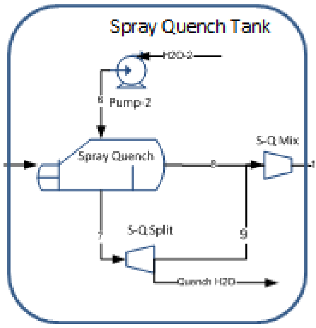


Figure 10 Diagram of overall spray quench tank unit operation

In addition, Table 12 provides a summary of material and energy balances related to the spray quench tank.

Table 12 Material & energy balances for spray quench unit operation

Spray Quench Tank		
	In	Out
Mass Flow (kg/hr)	2.19E+05	2.19E+05
Enthalpy Flow (kJ/hr)	-1.24E+08	-2.18E+08
Heat Duty (kJ/hr)		-9.38E+07

Solid Waste Removal

In the gasification of biomass process, solid waste is generated in the solar reaction step. This solid waste must be removed before the syngas can be further reacted into methanol. The most common method for removing solid waste in a syngas process is a cyclone. This technique is similar to a centrifuge in that it utilizes rotational effects to separate dense objects (solid waste) from less dense objects (syngas). Stream 10, containing solid waste (ash), enters the cyclone at the top and is separated from the desired product. A diagram depicting the cyclone operation is seen in Figure 11.

Figure 11 Diagram of a typical cyclone

As the gas containing solid particles travels down the cyclone at a relatively high velocity, a spiral pattern is formed. The centrifugal force resulting from the spiral force causes particles with a large density to hit the wall and fall out of the cyclone. The gas with less inertial force than the solid waste is forced out the top of the cyclone, thus attaining the desired separation.

A diagram of the solids waste removal is depicted in Figure 12.

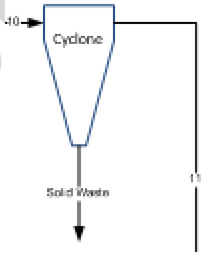


Figure 12 Diagram of cyclone unit operation

Ash is removed in the cyclone and exits in the solid waste stream to solid waste treatment. Syngas containing negligible ash exits the cyclone off the top in Stream 11. Table 13 provides a summary of all cyclone material and energy streams.

Table 13 Summary of material & energy streams for cyclone unit operation

Solids Waste Removal (Cyclone)

	Stream	Component	Molar flow (kmol/sec)	Composition (mol%)	Overall Enthalpy Flow (kJ/hr)	T (K)	Pressure (bar)
In	10	CO	0.5652	0.3076	-2.52E+08	483.15	35
		H_2	1.2171	0.6625			
		H_2S	0.0000	0.0000			
		N_2	0.0126	0.0069			
		HCl	0.0012	0.0007			
		CO_2	0.0050	0.0027			
		methanol	0.0039	0.0021			
		water	0.0214	0.0117			
		cellulose	0.0000	0.0000			
		lignin	0.0000	0.0000			
		ash	0.0106	0.0057			
		total	1.8371	1.0000			
Out	Solid Waste	CO	0.0133	0.2482	-3.94E+07	58.7	35
		H_2	0.0285	0.5346			
		H_2S	0.0000	0.0000			
		N_2	0.0003	0.0056			
		HCl	0.0000	0.0005			
		CO_2	0.0001	0.0022			
		methanol	0.0001	0.0017			
		water	0.0005	0.0094			
		cellulose	0.0000	0.0000			
		lignin	0.0000	0.0000			
		ash	0.0106	0.1978			
		total	0.0534	1.0000			
	11	CO	0.5519	0.3094	-2.13E+08	58.7	35
		H_2	1.1886	0.6664			
		H_2S	0.0000	0.0000			
		N_2	0.0123	0.0069			
		HCl	0.0012	0.0007			
		CO_2	0.0049	0.0028			
		methanol	0.0038	0.0021			
		water	0.0209	0.0117			
		total	1.7837	1.0000			

In addition to the composition summary for the cyclone material streams, Table 14 provides the material and energy balances for the cyclone

Table 14 Material & energy balances on cyclone unit operation

Cyclone		
	In	Out
Mass Flow (kg/hr)	2.19E+05	2.19E+05
Enthalpy Flow (kJ/hr)	-1.24E+08	-2.52E+08
Heat Duty (kJ/hr)		-1.28E+08

Zinc Oxide Fixed-Bed Reactor

The final product leaving the upstream process should be virtually free of all contaminants including: sulfur, chlorine, and ash. These contaminants can cause significant problems in the downstream production of methanol. The necessary desulfurization and de-chlorination takes place in the fixed-bed zinc oxide reactor (ZnO react) where hydrogen sulfide (H_2S) and hydrogen chloride (HCl) are removed from the syngas. Hydrogen sulfide is both corrosive and highly toxic, therefore it is essential that all traces are removed from the syngas. The adsorption of H_2S onto ZnO follows the following stoichiometric reaction where 100% conversion of H_2S is assumed:

$$ZnO(s) + H_2S \rightarrow ZnS(s) + H_2O$$

In addition to hydrogen sulfide removal, it is also important to remove hydrogen chloride from the crude syngas. Hydrogen chloride is not only reactive but it is also corrosive and extremely toxic. Corrosion as a result of improper HCl removal can cause major problems in the downstream operating equipment and is considered a hazard to operators and the environment. The removal of HCl in the fixed-bed reactor is governed by the following stoichiometric equation where 100% conversion of HCl is assumed:

$$ZnO(s) + 2HCl \rightarrow ZnCl_2(s) + H_2O$$

A diagram of the fixed-bed ZnO reactor is seen in Figure 13. In reality, all chlorine and sulfur would be adsorbed to the zinc inside the fixed-bed therefore leaving small traces of contaminants in stream 12. However, in order to simulate the fixed-bed in Aspen Plus™, a flash drum separator is used downstream from the fixed-bed for removal of any zinc contaminants.

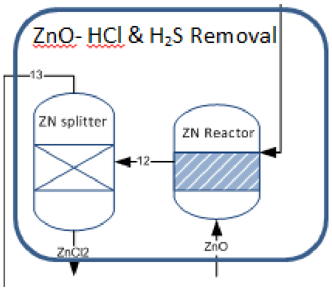


Figure 13 ZnO fixed-bed unit operation

Table 15 summarizes the properties and compositions of streams related to the fixed-bed.

Table 15 Summary of material streams related to zinc oxide fixed-bed reactor

ZnO fixed-bed reactor (HCL & H_2S removal)

	Stream	Component	Molar flow (kmol/sec)	Composition (mol%)	Overall Enthalpy Flow (kJ/hr)	T (K)	Pressure (bar)
In	ZnO	ZnO	0.0014	1.0000	-1.75E+06	298.15	1.013
	11	CO	0.5519	0.3094	-212960000	58.7	35
		H2	1.1886	0.6664			
		H2S	0.0000	0.0000			
		N2	0.0123	0.0069			
		HCl	0.0012	0.0007			
		CO2	0.0049	0.0028			
		methanol	0.0038	0.0021			
		water	0.0209	0.0117			
		total	1.7837	1.0000			
Out	13	CO	0.5519	0.3095	-2.13E+08	483.15	35
		H2	1.1886	0.6666			
		H2S	0.0000	0.0000			
		N2	0.0123	0.0069			
		HCl	0.0000	0.0000			
		CO2	0.0049	0.0028			
		methanol	0.0038	0.0021			
		water	0.0215	0.0121			
		total	1.7831	1.0000			
	ZnCl2	ZnO	0.0008	0.5542	-1.81E+06	483.15	35
		ZnS	0.0000	0.0158			
		ZnCl	0.0006	0.4300			
		total	0.0014	1.0000			

Material and energy balances related to the fixed-reactor are shown in Table 16 as follows.

Table 16 Material & energy balances for ZnO fixed-bed reactor

Fixed-Bed ZnO Reactor		
	In	Out
Mass Flow (kg/hr)	68668.057	68668.03
Enthalpy Flow (kJ/hr)	-2.15E+08	-2.15E+08
Heat Duty (kJ/hr)	0	

Raw Methanol Production

After crude syngas is purified from sulfur and chlorine contaminants in the ZnO fixed-bed reactor, it is reacted downstream in the methanol reactor. The final product in the upstream process is often referred to as dirty methanol. The raw methanol is then sent downstream to a holding tank before it is purified via distillation. The methanol reactor used in this process operates at a temperature of 270 °C and a pressure of 80 bar to convert syngas to the methanol product, a valuable fungible fuel. Raw methanol production begins with compressing the effluent gas from 35 bar in the ZnO fixed-bed reactor to its reaction pressure of 80 bar. The compression system requires two stages with an inter-stage cooler in order to maintain its temperature.

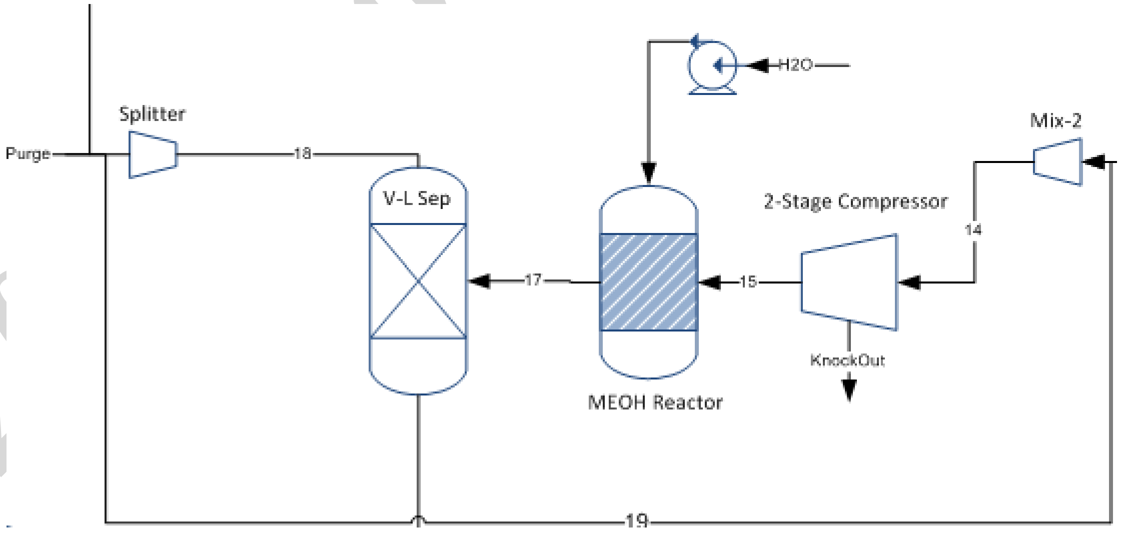


Figure 14 Methanol production process flow diagram

A diagram of the final methanol production step is shown in Figure 14. A table summarizing the compressor is shown in Table 17.

Table 17 Material & energy balances for compressor

Compressor		
	In (14)	Out (15)
T (K)	390.7404	338.7056
P (bar)	35	80
Mass Flow (kg/hr)	1.50E+05	1.49E+05
Enthalpy Flow (kJ/hr)	-4.49E+08	-4.65E+08
Heat Duty		-1.55E+07

After compression, the syngas stream enters the methanol reactor where the previously explained reactions go to 45% conversion with respect to their hydrocarbon component. The exit stream from the methanol reactor (17) is sent to a flash drum where it is decompressed to 35 bar resulting in a degree of separation since methanol is more volatile than water. The liquid stream (RAW-MEOH) leaving the bottom of the flash separator is then sent to the downstream process where it will be purified into a final product ready for consumption.

The vapor stream (18) is sent to a splitter where it is split and recycled into two different streams. Also, some of the vapor is purged and flared off of the splitter. The splitter recycles material back to the upstream process because the methanol reactor only achieves 45% conversion, therefore increasing efficiency. Stream 19 is sent to mix with stream 13 and stream 20 is returned to the beginning of the solar thermal reaction unit. Table 18 summarizes the compositions and properties of all streams related to the methanol reactor, and Table 19 provides a material and energy balance on the methanol reactor and flash drum.

Table 18 Material & energy balance for methanol reactor and flash drum

Methanol Reactor		
	In	Out
Mass Flow (kg/hr)	149224.1173	1470133
Enthalpy Flow (kJ/hr)	-4.65E+08	-6.98E+08
Heat Duty		-2.33E+08

Table 19 Summary of methanol production streams

Stream	13	14	15	17	18	19	20	Raw MeOH	Purge
Temp (K)	483.15	390.75	338.7	543.15	323.15	323.15	323.15	323.15	323.15
Pressure (bar)	35	35	80	80	35	35	35	35	35
Molar Flow (kmol/sec)	1.78312008	4.22789985	4.21606115	3.22979597	2.716612	2.4449512	0.2580782	0.51318352	0.0135831
Mass Flow (kg/sec)	18.9282752	41.7224029	41.4511437	41.4511437	25.32766	22.794891	2.4061274	16.1234871	0.1266383
Component Flow (kmol/sec)	-	-	-	-	-	-	-	-	-
CO	0.5519	1.09058376	1.09058376	0.60217934	0.598524	0.5386719	0.0568598	0.00365497	0.0029926
H_2	1.1886	2.95190842	2.95190842	1.96075556	1.959423	1.7634804	0.1861452	0.0013329	0.0097971
N_s	0.0123	0.11721967	0.11721967	0.11720778	0.116536	0.1048825	0.0110709	0.00067163	0.0005827
CO_2	0.0049	0.00538728	0.00538728	0.00053827	0.000508	0.0004568	4.82E-05	3.07E-05	2.54E-06
Methanol	0.0038	0.04076642	0.04076642	0.52981588	0.041067	0.0369603	0.0039014	0.4887489	0.0002053
Water	0.0215	0.02203428	0.02203428	0.01929913	0.000555	0.0004993	5.27E-05	0.01874436	2.77E-06

Downstream Methanol Purification

The second stage in the solar-thermal conversion of biomass to methanol is a downstream methanol purification process. The downstream process takes raw methanol produced upstream and converts it to fuel-grade methanol (99.97%) downstream. Since the upstream process is constrained by sunlight availability, it runs approximately 8 hours a day and produces a large volume of raw methanol, while the downstream process runs 24 hours a day to purify the resulting product. As a result of the difference in operating times and volume through-put, a large storage tank collects the accumulation of methanol in the system. Although the storage tank accounts for a decreased volumetric flow-rate out of the distillation column in real life, Aspen HYSYS™ simulates flow rates based on steady state assumptions. Therefore, the program assumes the upstream product is flowing 24 hours per day and the storage tank does not retain two-thirds of the flow. As a result, a splitter is added after the holding tank to divert 66.67% of the volumetric flow for proper simulation. Figure 15 shows the overall simulated process flow diagram for the downstream methanol purification process.

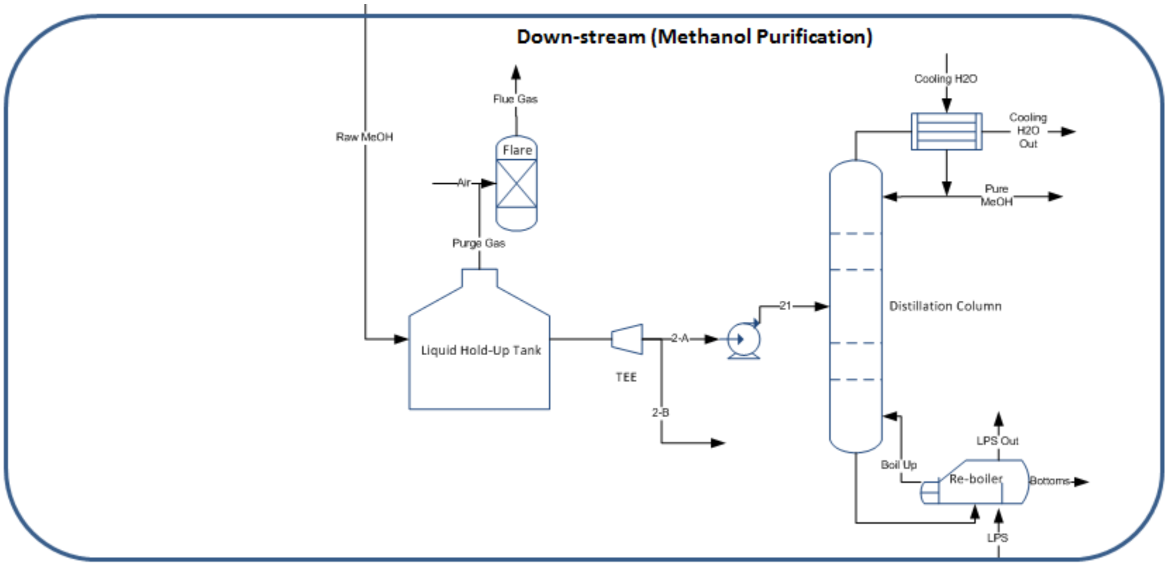


Figure 15 Process Flow Diagram for downstream purification of methanol

In real life, the tee is included as a safety precaution in the event of tank overflow. Once the raw methanol is sent to the holding tank operating at atmospheric pressure, volatile components are purged off the tank and are flared off. Table 20 summarizes the material and energy balances related to the flare tower.

Table 20 Material & energy balances for flare tower

Flare				
Stream	Purge Gas	Air	Flue Gas	Q
T(°C)	50	32.2	1093	
P(kPa)	101.3	101.3	101.3	17310004
Total Mass Flow (kg/hr)	935	5802	6737	
Enthalpy flow (kJ/hr)	-4639063.37	-746918	-1.2E+07	
Mass Composition (wt%)				
CO	0.408	0	0.1426	
H_2	0.0092	0	0.0032	
N_2	0.0485	0.7532	0.5069	
CO_2	0.0043	0.0152	0.0114	
methanol	0.5283	0	0.1846	
water	0.0017	0	0.0006	
O_2	0	0.2316	0.1507	

The outlet liquid stream from the proceeding unit operation is sent to a pump where the pressure is increased to 3 atm before distillation. Table 21 summarizes the material and energy streams related to the pre-distillation pump.

Table 21 Material & energy balance for Pump-3

Pump-3		
Stream	2a	21
T(°C)	50	50
P(kPa)	101.3	304
Total Mass Flow (kg/hr)	17359.6	17359.6
Enthalpy flow (kJ/hr)	-1.3E+08	-1.3E+08
Mass Composition (wt%)		
CO	0.0001	0.0001
H_2	0	0
N_2	0	0
CO_2	0	0
methanol	0.9792	0.9792
water	0.0207	0.0207
O_2	0	0

The exit stream discharges from the pump into the distillation column where methanol reaches its final purity. At this point the composition entering the column is mostly methanol and water. Therefore the distillation step was considered to be a simple binary distillation between water and methanol. At a pressure of 3 atm the pressure of feed to the distillation column, the boiling point of water and methanol is 120°C and 85°C respectively. With a temperature difference of 35°C between boiling points, separation between both components is feasible via distillation.

The desired separation requires 16 column stages, a total condenser, and a re-boiler. Table 22 summarizes the material and energy balance streams related to the distillation column.

Table 22 Material & energy balances for distillation column

Distillation			
Stream	21 (Feed)	MeOH	Bottoms
T(°C)	50	79.68033	130.4
P(kPa)	304	206.8	275.8
Total Mass Flow (kg/hr)	17359.6	16996.27	363.3
Enthalpy flow (kJ/hr)	-132672125	-1.2E+08	-5562744
Mass Composition (wt%)			
CO	0.0001	0.0001	0
H_2	0	0	0
N_2	0	0	0
CO_2	0	0	0
methanol	0.9792	0.9998	0.0145
water	0.0207	0.0001	0.9855
O_2	0	0	0

VIII. Process Description & Equipment Specifications

In this section we provide an overview of each major piece of equipment used in the methanol production process. Specifically, the unit operations are fully designed in order to estimate capital requirements for the plant's construction. The detailed calculations used to size and cost the equipment are found in Appendix C. The following sections summarize the results of these calculations.

High Temperature Solar Thermal Biomass Gasification

After processing the feed streams, they are fed into a solar-thermal reactor which converts methane, biomass, and steam to a high quality synthetic gas (syngas) in a solar thermo-chemical process known as gasification. The heat that powers the reaction enters the solar reactor through an aperture that is surrounded by secondary concentrators which guide the solar radiation reflected from a field of mirror-like heliostats in a process not all that different to the one we used as children to fry ants using a magnifying glass.

For a net energy requirement of Q_{solar} = 189.27 MW[14] needed to power the solar-thermal reactor, the optimal solar field design is calculated using simulations for multiple-field, single reactors at three different solar concentrations (2000, 4000, and 8000 suns).[15] In order to select the most cost effective design, the energy required to power the gasification reaction and the operating temperature is used to calculate the optimal tower height that yields the minimal total cost of the solar equipment. The simulation calculates the heliostat area, the compound parabolic concentrator (CPC) surface area, the number of towers and land area needed. Assuming a yearly net energy need of 553GW-hr to power the gasification of the feeds, the cost of the solar equipment is minimized at a height of 187.5 m using a 4000x concentration strength with an annual efficiency of 0.402 assuming 2920 hrs of operation a year in Daggett, CA. For detailed calculations consult Appendix B: Optimal Solar Field Calculations.

Heliostat Field

The heliostats reflect solar radiation from their shiny surfaces towards a central receiver. Due to the cost of the materials used to manufacture the heliostats, they represent a significant portion of the total capital investment.

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[14] The amount of energy needed to power the process. See section on Solar Reactor Energy Requirement, Approach Calculations

[15] Provide by Mr. Allan Lewandowski

The cost of the heliostats is assumed to be $126/m^2, the area of which is calculated using the simulation spread sheet provided by Mr. Lewandowski. This results in a total heliostat area of 492,777 m^2 for an installed price of $62,089,850 (CE = 575) in 2008, by far the most expensive component of the solar equipment and for that matter of the whole production facility. The purchase cost in 2010 is calculated using a CE = 556, for an installed price of $60,038,186.

$$C_P = \$62{,}089{,}850\left(\frac{556}{575}\right) = \$60{,}038{,}186$$

The heliostats are equipped with small motors that direct the solar radiance reflecting off their mirrored surfaces towards the apertures of the solar-thermal reactor given the position of the sun.[16] The heliostat fields are arranged around a central receiver as shown in the following figure.

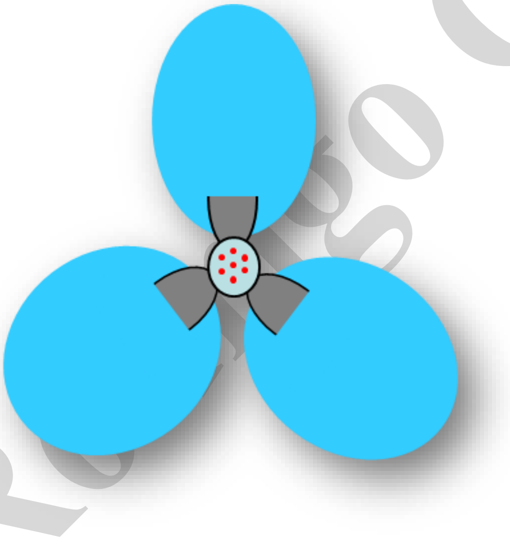

Figure 16 Multiple Field, Single Reactor Concept[17]

The land area required for the heliostat fields is also obtained from the spread sheet which gives a total of 275 acres. At a cost of $1000/acre in Daggett, California, the cost of the required land for the solar reactor and surrounding heliostat fields will be $275,000.

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[16] These are also known as "two-axis tracking parabolic mirrors" (19)

[17] Source: "Overview of Solar Thermal Central Receiver Field Design". Presentation given by Allan Lewandowski on November 4, 2010

Secondary Concentrator

In order to maximize the efficiency of the solar-thermal reactor system, the radiation reflected from the heliostats is directed towards the hexagonal entrance apertures using secondary concentrators made up of rectangular units as seen in the figure below (14). Concentrators are usually made of glass due to the solarization effects produced by UV radiation which result in a loss of transmission at the high operating optical power (15).

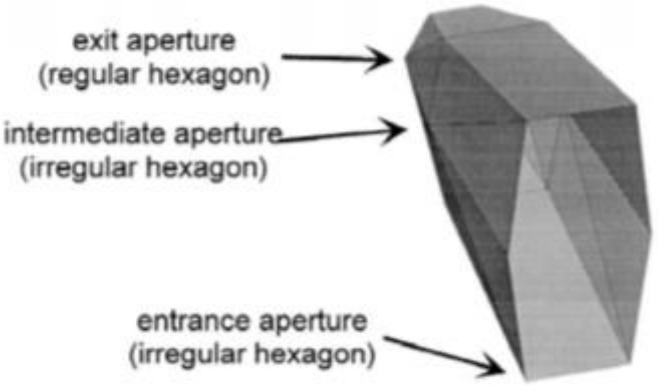

Figure 17 Concentrator with Hexagonal Aperture and Plane Facets

The cost of the secondary concentrator is assumed to be 10 times the price of the heliostats per m^2 at 639 m^2 for a total cost of \$805,140 (CE = 575) in 2008.The purchase cost in 2010 is calculated using a CE = 556, for an installed price of \$777,952.

$$C_P = \$805{,}140\left(\frac{556}{575}\right) = \$777{,}952$$

Central Receiver and Tower

The solar-thermal reactor is housed inside a central receiver which sits atop a tower. As the name implies, the central receiver collects all the solar radiation reflected off of the heliostats and is situated in the middle of three heliostat fields as shown in Figure 16. The following figure is a simple diagram of the overall receiver and tower design. The tower is stationary, hence the need for motorized heliostats that move in relation to the sun.

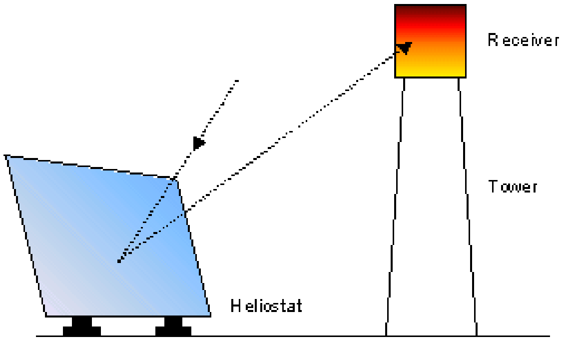

Figure 18 Central Solar Receiver Conceptual Diagram

The tower is priced given the correlation provided in the problem statement from a DOE study as shown below. The solar field simulation calculates that two towers are needed at the optimized height of 187.5 m given the net energy requirements.

$$y = \$1.41(600000 + 17.72x^{2.392})$$

Where y is the total installed cost in dollars and x the height of the tower in meters in 2008 (CE = 575). For two towers in 2010 (CE = 556), the total installed cost of the central receiver and tower is calculated to be $14,860,894.

$$C_P = \$15{,}368{,}731\left(\frac{556}{575}\right) = \$14{,}860{,}894$$

Solar-Thermal Reactor

The solar reactor itself operates at a high temperature of 1450 °C and a pressure of 35 bar. The high temperature is justified by the formation of high molecular weight tars when operating at lower temperatures. High molecular weight tars decrease the efficiency of the system and decrease yield (16). In order to withstand high operating temperatures, the reactor is made of silicon carbide tubes which will be custom made at a significant cost of approximately $1,000/ft. These are sized to ensure a design specification of approximately 500 KW/m^2 of heat flux delivered directly to the tubes for a calculated Q_{solar} = 189.27 MW. The carbide tubes are housed in a conventional steel cavity (17) filled with alumina insulation tiles which minimize heat loss to the surroundings. Studies show that approximately 50% of the energy loss is a result of conduction through the reactor walls and 41% is the result of re-radiation through the aperture; therefore insulation and a small aperture are desired (18).

As a result of the reactor's size and its intermittent use due to the availability of sunlight, it is desired that the interior of the reactor be sustained at 1450 °C. This is required for operation due to the loss in production that results in a large waiting time for the reactor to re-heat on a daily basis. Therefore, the reactor is fitted with shutters that close after each use which helps maintain the desired temperature through the night. In addition, a small electric heater is installed which can quickly heat the reactor to the desired operating temperature before start-up every day which ensures maximum efficiency (19).[18]

The volume of the reactor is sized using a residence time of 1 s (16) and a volumetric flow rate of 7.43 m^3/s (calculated by Aspen Plus™) for a total volume of 7.43 m^3 which is calculated by the following equation.[19]

$$Volume_{SR} = \tau \times \dot{V}$$

Given this calculated reactor volume, heat flux specification, silicon carbide tube diameters, the length of the reactor tubes can be calculated. Microsoft EXCEL™ was used to solve for the SiC tube length given the previous specifications and by minimizing the heat flux delivered to the tubes. A heat flux of 545.19 KW/m^2 is very close to the desired 500 KW/m^2 and is quite reasonable given that some of the radiation is lost. The number of tubes per tower is 72 giving an estimated total of 144 tubes which are arranged in a conformation that maximizes solar reactor efficiency. The following table summarizes the silicon carbide tubes. For detailed calculations consult Appendix C.

Table 23 Silicon Carbide Tube Specifications

Parameter	Value	Unit	Description
Di	4.5	in	Inner diameter
Do	6	in	Outer diameter
L	5.04	m	Calculated Length of single SiC tube
L_{SiC}	5.2	m	Tube Length + 3% Installation length
Vol_{SR}	7.44	m^3	Volume Solar Reactor
SA	347.16	m^2	Outer SiC tube surface area
Flux	545.19	KW/m^2	Flux delivered to tubes

The silicon carbide tubes are priced at a cost of $1,000/ft. Therefore, the price of 144 tubes at a length of 5.2 meters each totals to a price of $2,456,693.

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[18] It should be noted that when the heliostats are not in use they should all be moved so as not to face the apertures. This prevents any damage extending the life of the equipment.

[19] Where τ is the residence time in seconds, and $\dot{V}$ is the volumetric flow rate

The cost of the solar reactor is determined using information from literature on solar-thermal reactors used for hydrogen production from water, a similar process. The solar power input into the solar reactor is 90 MW and the cost for the solar receiver-reactor including any peripheral equipment is $7,000,000 in 2002 (CE = 396). The total bare module cost for the needed 189.27 MW delivered to the solar reactor in 2010 (CE = 556) using a cost component n = 0.6 is calculated to be $15,352,439 as shown by the following equation.

$$C_P = \$7{,}000{,}000\left(\frac{90\ MW}{189.27\ MW}\right)^{0.6}\frac{556}{396} = \$15{,}352{,}439$$

For informational purposes the area of the aperture can be related to the width and height via the following equations.

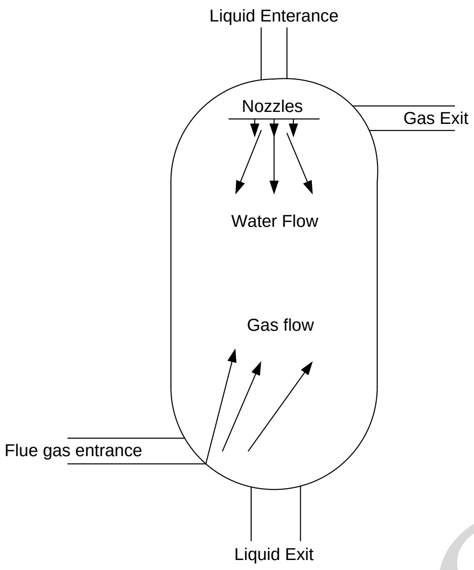
$$Area_{hex} = \frac{\sqrt{3}}{2}W^2$$

$$L = \sqrt{\frac{2Area_{hex}}{3\sqrt{3}}}$$

Spray Quench Tank & Water-Gas Shift Equilibrium

Spray Quench Tank

After the process gas exits the solar reactor, it must be cooled. A relatively inexpensive way to cool a hot process gas is to quench the gas with a mist of water droplets. As the high temperature gas comes into contact with the water droplets, energy is rapidly transferred from the gas to the liquid. As the liquid water temperature increases resulting in vaporization, the newly vaporized water joins the process gas stream as steam. Water has a very high latent heat of vaporization (44 kJ/mol at 25 °C and 1 atm). This high heat of vaporization allows for a relatively small amount of water needed to absorb the vapor’s energy which has a much lower heat capacity.



As seen in the figure above, hot gas enters the tank at the bottom and flows upward, exiting the top of the tank. Water enters an array of spray nozzles at the top of the tank and excess water exits the bottom of the tank as liquid, thus making the flow countercurrent. Energy transfer is driven primarily by convection. The following equation describes the residence time of gas within the spray tank:

$$\theta = \rho_l \lambda D^2 / 8 k_g \Delta T$$

pl	995	kg/m^3	Density of liquid droplet
lambda	32081624	j/kg	Liquid heat of vaporization found using HYSYS
Do	0.0005	m	Droplet diameter
kg	0.24	j/msk	Thermal conductivity of gas. Found in HYSYS
inlet T gas	1073.15	K	
inlet T liquid	305.3722	K	
outlet T gas	483.8889	K	
outlet T liquid	490.3675	K	
D_{Tg}	589.2611	K	Change in gas temperature
D_{Tl}	184.9953	K	Change in liquid temperature
ΔT	348.9445	K	log mean temperature between drop and gas
Theta	11.9	S	Evaporation time of droplets and residency time
Water flow rate	41.11	kg/s	
Gas flow rate	19.12	kg/s	

The spray quench tank is a 2m x 7.96m cylindrical tank. It is rated for 5000 kPa, well above the 3500 kPa that this unit process is assumed to operate. It is constructed out of Nickel alloy due to the highly corrosive contents of the flue gas. Adjusting for inflation, the cost of the Quench tank is $487,399.75.

Solid Waste Removal

Hydro-Cyclone

Once the synthesis gas has been cooled by the spray quench tank, it enters a hydro-cyclone which removes primarily ash and other solids from the stream. Due to the small particulate size, a reverse flow gas/solid hydro-cyclone is best suited for this unit operation. A high efficiency Stairmand cyclone is used to model the dimensions and specification. The scale up rules for a high efficiency cyclone requires the use of Euler's number of 320 and a Stokes number of 1.4 x 10^{-4} to find the characteristic flow velocity through the cyclone, as well as the inlet diameter Di. This can be done via the following equation:

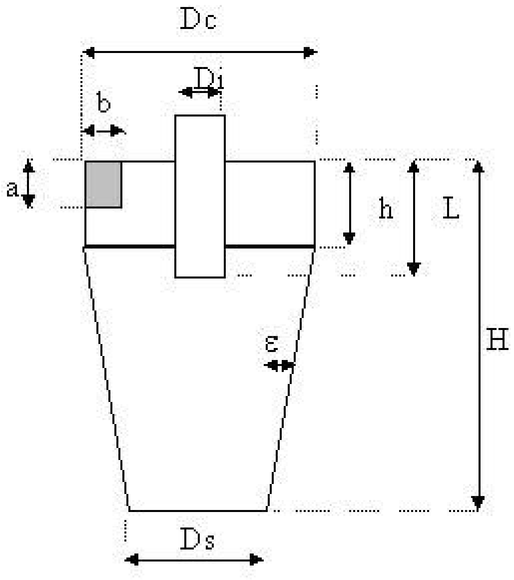
$$Eu = \frac{\Delta P}{(\frac{\rho_f u^2}{2})}$$

$$v = \frac{4q}{\pi D^2}$$

The characteristic velocity (v) through the cyclone is 5.67 m/s which results in an inlet diameter of 0.69 m. Other dimensions can be found in Table 24 below.

Table 24 Hydro-Cyclone Design Parameters

Geometries	Dimension Relative to Di	Dimension
H	4	2.75
h	1.5	1.03
Ds	0.375	0.26
L	0.5	0.34
b	0.2	0.14
a	0.5	0.34
Di	0.5	0.34



Cyclones do not act like size-exclusion filters which remove 100% of the particles that are too large. Rather, cyclones are designed based on the viscosity and momentum of the particles flowing through them which ultimately affect the desired separation. The inlet flow enters through the gray area (a x b) at a high speed. Small particles (gas) follow a circular path down the sides of the cyclone, and then up exiting near Di due to inertial differences. Larger particles hit the sides of the cyclone and fall to the bottom exiting near Ds. Separation efficiency is directly related to size of particles being separated. Using Stokes number, we can calculate the size of the particles which are being separated with 50% efficiency.

$$St = \frac{{x_{50}}^2 \rho_p v}{18 \mu D i}$$

For this cyclone, x is 2.01 µm and is significantly smaller than the smallest process particle size of 150 µm. Using this information, the Grade efficiency was calculated via the following equation:

$$G(x) = \frac{\left[\frac{x}{x_{50}}\right]^2}{\left[1 + \left(\frac{x}{x_{50}}\right)^2\right]}$$

In this equation the grade efficiency is 99.98% meaning that almost 100% of the smallest particles in our system will be removed.

In ASPEN Plus™, the simulated operating temperature of the cyclone is 210 C, the pressure is 35 bar and the total flow is 19.42 kg/s. Despite the presence of corrosives which would suggest that the unit be made out of nickel alloy, we suggest the use of stainless steel as abrasion in cyclones tends to be extremely high. Use of the softer nickel alloy could force the plant to replace the cyclone often. The 2010 cost of the cyclone is $11,866.31 adjusted for the additional cost of stainless steel and inflation.

Chlorine and Sulfur Removal over a Zinc Catalyst

Zinc Oxide Bed

The desulfurization and de-chlorination of the process stream occurs before the production of methanol. The adsorption of sulfur and chlorine takes place on a packed zinc oxide bed tubular reactor. The solid products including: zinc chloride and zinc sulfide cannot feasibly be regenerated during the process (20). Therefore, the bed is sized to adsorb the quantities of species to be removed until an opportune time. For simplification purposes we assume 100% removal of the hydrogen sulfide and hydrogen chloride via the following reactions with zinc oxide which produces a harmless water vapor byproduct.

$$ZnO_{(s)} + H_2S \rightarrow ZnS_{(s)} + H_2O$$

$$ZnO_{(s)} + 2HCl \rightarrow ZnCl_{2(s)} + H_2O$$

The ZnO bed is sized to remove all of the chlorine and sulfur the plant produces during full production over a three year period. In order to calculate the reactor volume, we will develop an algorithm that can be entered into a multi-differential equation solver such as POLYMATH™. Since we have already presented the chemical equations that describe the reactions occurring inside the reactor, we will now write a mass balance for each gaseous species and will neglect the species that are in the solid phase. For component i, the mole balance with respect to the catalyst weight is as follows.

$$\frac{dF_i}{dW} = r'_i$$

Where F_i is the molar flow, and r'_i is the reaction rate per unit weight of catalyst. This quantity is related to the rate of reaction per unit volume through the bulk density of the catalyst particles, ρ_b as shown in the following equation.

$$-r_i = \rho_b(-r'_i)$$

For simplification purposes, we assign a letter to each chemical species: A corresponds to water, B, and C to hydrogen sulfide and hydrogen chloride respectively. The letter I takes into account all of the other non-reacting gaseous species. Now we are free to write the net rates of reaction for species A, B, and C which are:

$$r'_A = r'_{1A} + r'_{2A} = k_1 C_B + 2k_2 C_C$$

$$r'_B = r'_{1B} = -k_1 C_B$$

$$r'_C = r'_{2C} = -k_2 C_C$$

The rate constants for the reactions are calculated for an operating temperature of 225 ℃ as calculated by Aspen Plus™ and take the form of the Arrhenius equation, which were located in the literature for reactions 1 and 2 respectively (21) (22).

$$k_1 = 0.0147 exp\left({}^{11842}/_{RT}\right)$$

$$k_2 = 3.98454 \times 10^{-5} exp\left({}^{4.88 \times 10^4}/_{RT}\right)$$

Where R is the gas constant and T is the temperature in K. Since the reactions occur in the gas phase, we can use a form of the ideal gas equation to describe the concentration of each species. The general form of the equation takes into account changes in the absolute temperature and pressure.

$$C_j = \frac{F_{T0}}{\upsilon_0}\left(\frac{F_j}{F_T}\right)\frac{P}{P_0}\frac{T_0}{T} = C_{T0}\left(\frac{F_j}{F_T}\right)\frac{P}{P_0}\frac{T_0}{T}$$

Where

$$F_T = \sum_{j=1}^{n} F_j$$

And

$$C_{T0} = \frac{P_0}{RT_0}$$

For simplification purposes we will assume an isothermal system (T = T_0). For the three species A, B, and C the stoichiometry is given by the following equations:

$$C_A = C_{A0}\frac{\left(1 + {}^{F_{B0}}/_{F_{A0}}\,X + {}^{1}/_{2}\,{}^{F_{C0}}/_{F_{A0}}\,Y\right)}{(1 + \varepsilon_1 X + \varepsilon_2 Y)}\frac{P}{P_0}\frac{T_0}{T}$$

$$C_B = C_{B0}\frac{(1 - X)}{(1 + \varepsilon_1 X + \varepsilon_2 Y)}\frac{P}{P_0}\frac{T_0}{T}$$

$$C_C = C_{C0}\frac{(1 - Y)}{(1 + \varepsilon_1 X + \varepsilon_2 Y)}\frac{P}{P_0}\frac{T_0}{T}$$

Where X and Y are the extent of reactions for 1 and 2 respectively.

Given that there are two reactions, only two molar balances are required. From the extents of reaction with respect to catalyst weight, W, we arrive at the following equations for species B and C.

$$F_{B0}\frac{dX}{dW} = -r'_B = k_1 C_B$$

$$F_{C0}\frac{dY}{dW} = -r'_C = k_2 C_c$$

When combined with the stoichiometric calculations, the result yields the following equations for an isothermal system:

$$F_{B0}\frac{dX}{dW} = k_1 C_{B0}\frac{(1 - X)}{(1 + \varepsilon_1 X + \varepsilon_2 Y)}\frac{P}{P_0}$$

$$F_{C0}\frac{dY}{dW} = k_2 C_{C0}\frac{(1-Y)}{(1+\varepsilon_1 X+\varepsilon_2 Y)}\frac{P}{P_0}$$

Since the reaction takes place in a packed bed there will be pressure drop effects. In order to calculate the pressure drop we will use the Ergun equation for a packed porous bed.

$$\frac{dP}{dz} = \frac{-G}{\rho g_c D_P}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150(1-\phi)\mu}{D_P}+1.75G\right]$$

The first term inside the square brackets is dominant for laminar flow, while the second term is dominant for turbulent flow.

We define P/P_0 as y and express the Ergun equation as follows:

$$\frac{dy}{dW} = \frac{-\alpha}{2y}(1+\varepsilon_1 X+\varepsilon_2 Y)$$

$$\alpha = \frac{\beta_0}{A_c\rho_c(1-\phi)P_0}$$

$$\beta_0 = \frac{G(1-\phi)}{\rho_c g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P}+1.75G\right]$$

And simplify the molar balances as follows:

$$\frac{dX}{dW} = \frac{k_1}{\nu_0}\frac{(1-X)}{(1+\varepsilon_1 X+\varepsilon_2 Y)}y$$

$$\frac{dY}{dW} = \frac{k_2}{\nu_0}\frac{(1-Y)}{(1+\varepsilon_1 X+\varepsilon_2 Y)}y$$

Now that we have all of the necessary equations, we can enter them into a differential equation solver for a given reactor diameter, feed rates, and properties.

The following table gives the identities and flow rates calculated in the feed stream.

Table 25 Molar Feed Rates of Each Species into the ZnO reactor

Parameter	Value	Units	Description
FA0	20.9151	mols/s	Initial feed rate of species A
FB0	2.20E-02	mols/s	Initial feed rate of species B
FC0	1.19E+00	mols/s	Initial feed rate of species C
FI	1761.5853	mols/s	Feed Rate of inert species
FT0	1783.7168	mols/s	Total feed rate

The following parameters were used to calculate the mass of ZnO used in the reactor.

Table 26 Catalyst Physical Properties and Reactor Specifications

Parameter	Value	Units	Description
P_0	35	bar	Initial pressure
	3500	kPa	
v_0	2.11	m3/s	volumetric flow rate
phi	0.4	-	porosity (void fraction) = volume of void/total bed volume
1-phi	0.6	-	volume of solid/total bed volume
rho c	3140	kg/m3	Density of the Solid Particles
rho b	1884	kg/m3	Bulk Density
gc	1	-	Conversion factor (1 for SI)
Dp	0.004	m	Diameter of ZnO particle in the bed
mu	1.74E-05	kg/m/s	Viscosity of the gas passing through the bed
u	0.429	m/s	superficial velocity = volumetric flow/cross-sectional area of the pipe
D	2.5	m	Diameter of the pipe
Ac	4.908	m^2	Cross-sectional area of the pipe
rho	8.984247	kg/m3	Gas density
G	0.000156	kg/m^2s	Superficial mass velocity (rho * mu)

From this information and the known identity of the feed streams and the annual plant operation of 2920 hours,[20] the amount of sulfur and chlorine to be removed can be calculated. First the mass of the Chlorine

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[20] Annual Plant Operation provided in problem statement

and Sulfur to be removed were calculated using the feed rate into the ZnO reactor calculated using the Aspen Plus™ simulation by multiplying the feed rates of the different components by their respective molecular weights of the compound to be removed as shown in the following equation for sulfur.

$$F_S = F_A \times MW_S$$

Where F_S is the mass flow rate of sulfur through the reactor (g/s), F_A is the flow rate of the hydrogen sulfide (mol/s), and MW_S is the Molecular Weight of a Sulfur atom. This value is then added to the mass flow rate of the chlorine to be removed. ZnO has a weight pick up capacity of 0.4 in order to calculate the amount of ZnO needed for the bed the mass of both sulfur and chlorine that flows through the reactor is calculated for 3 years and divided by 0.4 as shown below.

$$Mass_{ZnO} = \frac{Mass_S + Mass_{Cl}}{0.4}$$

Now that we have the mass of ZnO for the reactor, the volume of the reactor is calculated using the density and bulk density of the ZnO pellets.

$$Reactor\ Volume = \frac{Mass_{ZnO}}{\rho_b}$$

Where the reactor volume is equal to the mass of the zinc oxide multiplied by its density. This gives us a reactor volume and given a column diameter, D_i, of 8 m. We can now estimate the height of the towers (m), Hc, that will be used to contain the ZnO pellets.

$$H_c = \frac{Vol_{ZnO}}{0.25 \times \pi D_i^2}$$

A height of 12 m is calculated. The reactor is constructed using nickel alloy as vertical column and prorated for up to 5000 kPa in order to minimize corrosion of the outer shell.. This has the advantage of making changing the catalyst easier, since the newest bed will always be rotated into the back. The bare module cost is given by the following equation using a cost exponent of 0.6 for the smaller diameter.

$$\mathrm{y} = \$(-150.794057377049\mathrm{x}^2 + 152273.30942623\mathrm{x} + 736512.55122950800)\left(\frac{556}{500}\right)\left(\frac{D_i}{4}\right)^{0.6}$$

Where y is the purchase cost of a column at the specified volume and x is the height of the columns in meters. The purchase cost is adjusted for a CE index of 556 for a total $1,492,518 for the fixed-bed reaction column. Earlier the mass of ZnO needed was calculated, and this can be multiplied by $0.20/kg for total cost of $1,346,465 for the ZnO catalyst. For detailed calculations consult Appendix B and Appendix D.

Raw Methanol Production

Multi Stage Compressor

After exiting the Zinc reactor and splitter, the synthesis gas must be compressed from 35 bar to 80 bar. This represents a fairly major technical challenge as maximum gas temperature cannot exceed 375 °F and compressors have a maximum discharge pressure that they are able to handle. All calculations are carried out using both absolute temperature and pressure. As an easy first approximation, we can assume that the compressor is a single stage unit. The process stream enters at 243.7 °F or 703 °R. Using the equation below, we find that the outlet temperature would be roughly 428 °F which is well above the 375 °F design specification.

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^a$$

In order to overcome this, we split the compressor into two sections and then cool the process stream in between. In order to design the most efficient system, we wish to approximately equalize the horsepower requirement of each stage to maximize efficiency. To do this, the equations are entered in excel, and solved with excel solver such that the two compression ratios are equal.

Theoretical Adiabatic Horsepower requirements are calculated with the following equation:

$$THp = SCFM \frac{T_1}{8130a} [\left(\frac{P_2}{P_1}\right)^a - 1] \quad (2)$$

The results from both the hand calculations as well as Aspen plus are summarized below.

From Hand calculations	Stage 1	Stage 2	Units
Inlet T	243.662725	150	F
Outlet T	330.333974	225.1609071	F
Inlet P	36.01325	54.01	Bar (abs)
Outlet P	54.01	81.01325	Bar (abs)
Compression Ratio	1.50	1.50	
THp	508247.1881	440749.6158	HP
Total Hp	948996.8038		

From Aspen	Stage 1	Stage 2	Units
Inlet T	363.968059	52.9150285	F
Outlet T	255.885332	80.0000034	F
Inlet P	36.01325	53.9282785	Bar (abs)
Outlet P	53.9282785	81.0132534	Bar (abs)
Compression Ratio	1.51185789	1.51580805	Unitless
HP	11213.3076	9763.0727	HP
Total Hp	20976.3803		

A reciprocating compressor is used to model this unit operation due to heads and flow rates associated with it. The compressor is made of carbon steel, and includes a drive, gear mounting, base plate and misc. auxiliary equipment. According to aspen plus, the power required is 15,642 kW. Accounting for both size scale-ups as well as inflation, the multi stage compressor costs $10,296,711.87.

Methanol Reactor

The conversion of syngas to methanol product occurs inside a fixed-bed reactor design and configuration over a highly efficient Cu/ZnO/Al_2O_3/ZrO_2 catalyst. This has been found to have selectivity for methanol of 94.1% (23). The methanol production rate has been found to be dependent on the adsorption of water and carbon dioxide on the catalyst and the equilibrium relationships of the fugacities (24) (25). Methanol synthesis is dependent on the following three equations.

$$CO + 2H_2 \rightarrow CH_3OH \qquad (1)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (2)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (3)$$

The reaction rates in moles per liter hour used for the model are given as follows and take into account the chemical equilibrium of the methanol reaction and the water-gas shift reaction (26).

$$r_1 = k_1\left(f_{CO} f_{H_2}^{2.5}\right)^{0.35} \frac{\left\{1 - \left(\frac{f_{CH_3OH}}{K_1 f_{CO} f_{H_2}^2}\right)^{0.8}\right\}}{1 + K_{CO_2} f_{CO_2} + K_{H_2O} f_{H_2O}}$$

$$r_2 = k_2 f_{H_2}\left(1 - \frac{f_{CO} f_{H_2O}}{K_2 f_{CO_2} f_{H_2}}\right)$$

$$r_3 = k_3 f_{CO_2} \frac{\left\{1 - \frac{f_{CH_3OH} f_{H_2O}}{K_3 f_{CO_2} f_{H_2}^2}\right\}}{1 + K_{H_2O} f_{H_2O}}$$

Where the reaction rate constants as a function of temperature (K) are given by:

$$k_1 = 1.03 \times 10^7 \exp(-\frac{16.6}{RT})$$

$$k_2 = 1.25 \times 10^{12} \exp(-\frac{28.8}{RT})$$

$$k_3 = 2.33 \times 10^7 \exp(-\frac{15}{RT})$$

The adsorption equilibrium constants as a function of temperature (K) are given by (20):

$$K_{CO_2} = 1.86 \times 10^{-9} \exp(-\frac{18.1}{RT})$$

$$K_{H_2O} = 1.06 \times 10^{-7} \exp(-\frac{16.7}{RT})$$

Where R represents the gas constant in cal/(g-mol K), and the equilibrium constants as a function of temperature (K) and pressure (atm) are given by:

$$K_1 = \frac{3.27 \times 10^{-13} \exp\left(\frac{11678}{T}\right)}{1 - \left(1.95 \times 10^{-4} \exp\left(\frac{17.03}{T}\right)\right) P}$$

$$K_3 = \frac{3.826 \times 10^{-11} \exp\left(\frac{6851}{T}\right)}{1 - \left(\left(1.95 \times 10^{-4} \exp\left(\frac{1703}{T}\right)\right) P\right)\left(1 - \left(4.24 \times 10^{-4} \exp\left(\frac{1107}{T}\right)\right) P\right)}$$

The identities of K_1 and K_3 are used to calculate the equilibrium relationship K_2 as follows:

$$K_2 = \frac{K_3}{K_1} = \frac{\frac{[CH_3OH][H_2O]}{[CO_2][H_2]^3}}{\frac{[CH_3OH]}{[CO][H_2]^2}} = \frac{[H_2O][CO]}{[H_2][CO_2]}$$

The reaction rates are dependent on the fugacities of the reacting species. The fugacity of component j is calculated given the relationship

$$f_j = \varphi_j x_j P$$

Where φ_j is the fugacity coefficient, x_j is the mol fraction, and P is the pressure in atmospheres. The fugacity coefficients are calculated using the Soave-Redlich-Kwong equation of state given below, as this relationship best corrects the non-ideal gas behavior observed inside the methanol reactor (27).

$$ln\varphi_i = \frac{1}{RT}\int_V^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - lnZ$$

$$Z = \frac{Pv}{RT} = \frac{v}{v - b} - \frac{a(T)}{RT(v + b)}$$

Where the parameters a and b are the mixing rules developed without use of interaction coefficients (27). These are calculated using critical temperatures and pressures and the acentric factors given in the table below.

$$a = \sum_i \sum_j y_i y_j \sqrt{a_i a_j}$$

$$b = \sum_i y_i b_i$$

Critical properties of species present in methanol production (28) are presented in the following table.

Table 27 Critical Properties of MeOH Reactor

Component	$P_{c,I}$ (bar)	$T_{c,I}$ (K)	$\nu_{c,I}$ (m^3 mol^{-1})	ω_i
CO	35.0	132.9	93.1	0.049
CO_2	7308	304.2	94.0	0.255
H_2	20.5	43.6	51.5	0
H_2O	220.5	647.3	56.0	0.344
CH_3OH	81.0	512.6	118.0	0.572

However, we can use the ideal gas law to simplify the problem by setting the fugacity coefficients equal to one, and using the following relationship.

$$x_j = \frac{P_j}{P}$$

Which results in the following simplification:

$$f_j = \varphi_j x_j P = \frac{P_j}{P} P = P_j$$

This ultimately results in a system of six differential equations, which will difficult to solve given the available computing power. Therefore, we will use a simplified model that incorporates a similar problem with an extremely close operating pressure of 82 bar, which shall be used to price the methanol reactor (29). The following table gives the specifications of the reactor that will be used to size the reactor in our study.

Table 28 MeOH Reactor Specifications

Parameter	**Value**
Tube inner diameter (mm), Dt	44.5
Tube outer diameter (mm), D0	48.5
Number of tubes	4801
Tube length (m), z	7260
Tube inlet temperature (˚C), T0	225
Shell steam temperature (˚C), Ts	250
Catalyst diameter (mm), Dp	6
Bed porosity (Φ), εB	0.4
Specific surface area (m2/g), av	80
Catalyst density (kg/m3), pB	1100
Feed flow rate (kmol/h), F t	40789
Inlet Pressure (bar)	82

Given this information we can calculate the mean residence time the feed is in the reactor and decrease the number of tubes in order to describe out flow rate, the following table gives the results of scaling this process down for our reactor. The following figure shows the Lurgi reactor that will be used in this process.

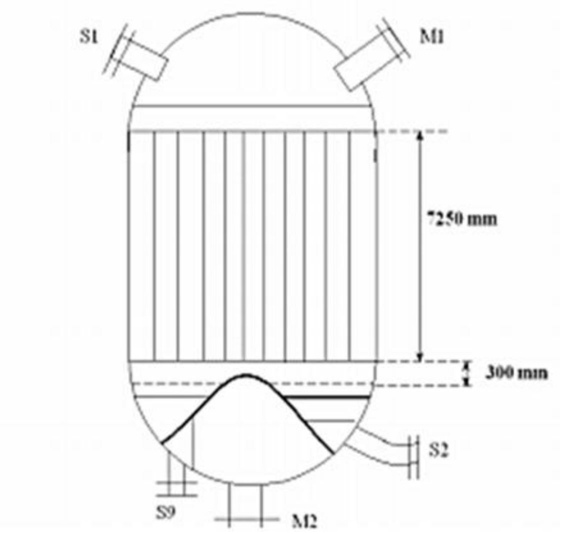

Figure 19 Lurgi Type Methanol Reactor Diagram

The methanol reactor is composed of thousands of very small tubes which help with the heat transfer that may affect the yield of the reaction. We shall use the ideal gas law to calculate a ratio, which shall be used to calculate the number of tubes required for this process. It should be noted that the tubes shall retain the same length and diameter so as to retain the velocity profiles, and heat transfer characteristics of the Lurgi type reactor.

$$Number\ of\ Tubes\ ratio = \frac{NV}{N_0V} = \frac{P_0FT}{PF_0T_0}$$

Where N is the number of tubes, V is the tube volume and therefore the same for both reactors, and P, F, and T are the pressure, flow rate, and absolute temperature respectively. The number of tubes was increased by 20 percent in order to ensure that the reactor is large enough for the process for a total of 2636 tubes. This can be done because the flow rate going through each of the small tubes of the reactor will not be changed if the number of tubes in the reactor is not changed. This is also used to calculate the total tube length of the reactor.

Methanol Reactor Costing

The methanol reactor is priced using the following equation used to price a multi-tube Lurgi type methanol reactor using the diameter and length of the reactor needed (30).

$$C_P = \$17640 * D^{1.066} L^{0.802}$$

The length of the reactor is sized as twenty percent larger than the tubes used in the Yusup study as recommended by Luyben (2010), for a length of 10.89 m. The diameter of reactor needs to take into account the spacing between the tubes which using a simple tube sheet layout program for similarly shaped heat exchangers in a factor of 2.035 greater than the surface area of the tube openings. From this area, the diameter is calculated to be 9.91 m. The total bare-module cost comes out to be $1,380,737 for the reaction vessel itself. Since the article was published in the year this study took place, no engineering index correction is applied For detailed calculations consult the section on the methanol reactor in Appendix B.

The catalyst used is a highly efficient $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst, which can be purchased for $10/kg. The amount of catalyst needed is calculated from the volume of the tubes in the Lurgi reactor assuming a catalyst density of 1100 kg/m^3. This comes out to be $196,473 for the catalyst.

Vapor-Liquid Flash Separator

The final step before crude methanol is sent downstream to a distillation tower is a flash separation drum. Flash separation drums are commonly used before a distillation column in order to cost-effectively pre-concentrate the desired product in the feed stream to its final separation (31). In the conversion of biomass into methanol process, the flash drum operating at a temperature of 50°C and a pressure of 35 bar is capable of achieving a substantial separation before distillation. In the V-L separator simulated by Aspen Plus™, the flash drum is capable of converting a mixture of 20 mole% methanol into a liquid product of 95 mole%. In order to size and cost the flash drum, the drum is modeled as a vertical pressure drum described in (32). Seider prices vertical pressure vessels based on diameter, height, weight, and operating pressure of the desired vessel. In order to determine the diameter and height of the V-L separator, the maximum vapor velocity is calculated via the Souders-Brown equation:

$$Vmax = K\left(\frac{d_L - d_V}{d_V}\right)^{0.5}$$

Where K, d_L, and d_V are 0.35, liquid density in lb/ft^3, and vapor density in lb/ft^3 respectively. From the liquid and vapor densities calculated by Aspen Plus™, the maximum vapor velocity in the flash drum is 2.78 ft/s. Since the flow rate of vapor into the drum is calculated by Aspen Plus™, the cross sectional area of the cylindrical drum can be calculated based off of the flow rate and maximum velocity in the following equation:

$$Q = V_{max} A$$

Once the cross sectional area of the drum is calculated, the diameter can be estimated from the simple geometry of a cylindrical vessel.

$$A = \pi \left(\frac{D}{2}\right)^2$$

With a calculated cross-sectional area of 23.1ft^2, the diameter of the vessel is estimated to be 5.43 ft. Once the diameter is estimated, the volume of the vessel is determined based on a liquid residence time (τ) of 5 minutes filling only half the volume of the entire drum. With the simulated outlet liquid flow rate (Q_L) in Aspen Plus™, the entire drum volume is calculated via the following equation:

$$Volume = \frac{Q_L \tau}{Liq.Vol\%}$$

Based on these assumptions, the vertical pressure vessel is estimated to have an internal volume of 450.1 ft^3. Based on a vertical cylinder model of the vapor-liquid separator, the height of the vessel is calculated to be 19.5 ft from the required volume and estimated diameter in the following equation:

$$V = \pi \left(\frac{D}{2}\right)^2 H$$

After the dimensions of the vertical pressure vessel are established, a price for platforms and ladders are calculated via Seider equation 22.56:

$$Cpl = 361.8(Di)^{0.73960}(L)^{0.70684}$$

With a diameter of 5.7 ft and a height of 18.3 ft, the price of platforms and ladders are estimated to be \$10,305. With the known operating pressure of 507.85 psig inside the separation vessel, a cylindrical shell wall thickness is calculated that will be able to safely handle the pressure inside the vessel. First however, as a precautionary safety measure; a design pressure is calculated which exceeds the actual operating pressure in Seider equation 22.61:

$$Pd = \exp[0.60608 + 0.91615\ln(P_0) + 0.0015655\ln(P_0)^2]$$

Operating at a pressure (P_0) of 507.85 psig, the design pressure (P_d) is calculated to be 586.77 psig. Based on the calculated design pressure, the shell thickness needed to safely operate at the design pressure is estimated based on Seider equation 22.60:

$$tp = \frac{PdDi}{2SE - 1.2Pd}$$

Where E is the fractional weld efficiency[21] (E = 0.85) and S is maximum allowable stress (S = 15,000 psi for -20-650°F) allowed by the shell wall. Using the calculated design pressure and vessel diameter estimate, the required wall thickness (t_p) is calculated to be 1.54 inches. Knowing the density of the carbon steel used as the material to base the cost (ρ = 0.284 lb/in^3), the weight of the vessel can be approximated by Seider equation 22.59:

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[21] Seider pg. 575

$$W = \pi(Di + tp)(L + 0.8Di)tp \times \rho$$

The weight of the vessel is calculated to be 28,163 lbs. With the weight (W) of the vessel calculated, the base cost of the vessel is estimated using Seider equation 22.54:

$$Cv = exp[7.0132 + 0.18255\, ln(w) + 0.04333\, ln(w)^2]$$

The cost of the vessel (C_v) is estimated to be $630,401 which does not account for the differences in material. To avoid corrosion, the actual flash separator will be constructed out of S.S 316. The additional cost of materials is accounted for by multiplying the estimated base cost by the material factor (F_m). The total purchase cost of the flash separator is then estimated by adding the cost of platforms and ladders to the factored price of the bare vessel. Since Seider estimates this vessel cost at CE = 500 (2006), inflation in 2010 is factored into the total bare module cost (CE = 556) (32).

$$Cost = (Cv \times (Fm\ (S.S.316))/(Fm\ (Carbon\ Steel))\ + Cpl) \times \left(\frac{I}{Ibase}\right)$$

Where F_m (S.S 316) = 1.7 and F_m (Carbon Steel) = 1

Accounting for materials of construction, inflation, and the price of platforms and ladders; the estimated cost of the V-L separator in 2010 is $ 1,203,170.

Downstream Methanol Purification

Downstream Storage Tank

A large storage tank is incorporated into the start of the downstream process to store crude methanol as it is made upstream. The tank is necessary to store crude methanol because the upstream process produces roughly 3 times as much that is distilled and purified on an hourly basis. The distillation column runs 24 hours per day to completely distill the crude methanol made upstream in 8 hours per day; this leaves a 16 hour hold up of raw material in the tank. In order to achieve the required 56 million gallons/year specification of pure methanol, 67.12 m^3/hr of crude product (calculated by Aspen Plus™) are fed in to the storage tank before it is distilled. With a known flow rate (Q) in m^3/hr and a residence time (τ) in hours, the volume of the tank can be estimated by the following equation:

$$Volume = \frac{Q \times \tau}{Liquid\,Vol.\%}$$

At a tank liquid level of 60% and a liquid residence time of 16 hours, the tank is expected to have a total volume of 1789.86 m^3. Furthermore, at an operating pressure of 101.3 kPa and a temperature of 50°C, the storage tank operates below the vapor pressure of the raw methanol mixture (6607 kPa calculated in Aspen HYSYS™) which allows volatile impurities to vaporize and purge through an outlet vapor purge stream. The volatile species purged out of the tank's vapor space are incinerated in a pyrolysis furnace which will be discussed in the following section. Allowing impurities to purge off in the tank serves as an additional purification step before methanol is fed to the distillation column at close to 96% molar purity. According to Seider table 22.32 for a spherical storage tank (0-30 psig); storage tanks are priced based on their size in gallons:

$$C_p = 60(V)^{0.72}$$

The spherical storage tank with a 472,524 gallon volume is expected to have a base price of $730,696. Since Seider formatted this cost equation for a CE of 500, inflation is factored into the price by multiplying by (556/500). In 2010, the storage vessel is estimated to cost $812,534.

Purge Gas Pyrolysis Furnace

The large storage tank located upstream from the distillation column purges a volatile mixture of hydrogen and hydrocarbons. In order to operate safely and comply with EPA environmental regulations, the purge gas stream cannot be purged directly to the atmosphere. Instead, the volatile components will be completely combusted with excess air. Full conversion of the volatile hydrocarbon mixture into CO_2 and water will be assumed to take place in a fired heater. Seider notes that "fired heaters are also used as reactors, such as reformers in petroleum refineries and for pyrolysis of organic chemicals" (Seider 582-583).

In order to price the fired heater unit, the pyrolysis furnace is modeled in Aspen HYSYS™ as a conversion reactor with the following stoichiometric reactions:

$$1.5CO + 0.5O_2 \rightarrow 1CO_2 \qquad \text{(100\% conversion of CO)}$$
$$H_2 + 0.5O_2 \rightarrow H_2O \qquad \text{(100\% conversion of } H_2\text{)}$$
$$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O \qquad \text{(100\% conversion of } CH_3OH\text{)}$$

An air stream with the composition of air (78% N_2, 21% O_2, and 1% CO_2) is fed to the pyrolysis furnace in a stoichiometric excess to ensure complete combustion of volatile components in the purge gas stream. Heuristic 30 in the Seider text says "typically, a hydrocarbon gives an adiabatic flame temperature of approximately 3,500° F… use excess air to achieve complete combustion and give a flue gas temperature of 2,000°F" (Seider 168). Therefore, in the conversion reactor modeled by Aspen HYSYS™, the effluent flue gas temperature is specified as 2,000°F to estimate the net duty required to react all the species. Seider prices fired heaters for special purposes in table 22.32 based on their net heat duty in BTU/hr. For a pyrolysis furnace constructed from carbon steel with a heat duty range of 10-500 million BTU/hr, Seider table 22.32 bases the cost of this unit via the following equation:

$$C_b = 0.65Q^{0.81}$$

The base cost for a pyrolysis furnace with a heat duty (Q) of 3.76E6 BTU/hr[22] is $137,781. However, because the heat duty is less than 10 million BTU/hr specified by the costing assumptions, the lower heat duty is accounted for with the economy of scale 0.6 factor:

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[22] Calculated using Aspen HYSYS™

$$C_{b_{actual}} = C_p\left(\frac{Q}{Qbase}\right)^{0.6}$$

Accounting for the differences in heat duty, the actual base cost of the pyrolysis furnace is \$76,661. Next, the materials of construction and inflation are accounted for by multiplying the adjusted base cost with a material factor of 1.7 for stainless steel and (556/500) for inflation:

$$C_p = C_{b_{actual}}(F_m)\left(\frac{I}{I_{base}}\right)$$

The purchase cost of this pyrolysis furnace constructed out of stainless steel in 2010 is \$144,921.

Methanol Distillation Column

The final step of the purification process is a 16 stage distillation column equipped with a total condenser and a partial re-boiler. Similar to Dr. Alwyn Pinto's patented 1980 methanol distillation process, 96% pure methanol will be fed at a volumetric rate of 25.02 m^3/hr into the distillation column. Fuel grade methanol (99.97%) will be recovered as distillate off the top of the column at a rate of 24.6 m^3/hr. A molar mixture of 99% water and 1% methanol flowing at 0.42 m^3/hr will be recovered as bottoms.

Condenser Pressure Estimate:

In order to design a distillation column capable of producing high purity methanol, Seider's methods for distillation design were employed. First, Seider's algorithm in Figure 20 Algorithm for Establishing Distillation Column Pressure and Condenser Type was utilized to determine the column pressure and condenser type.

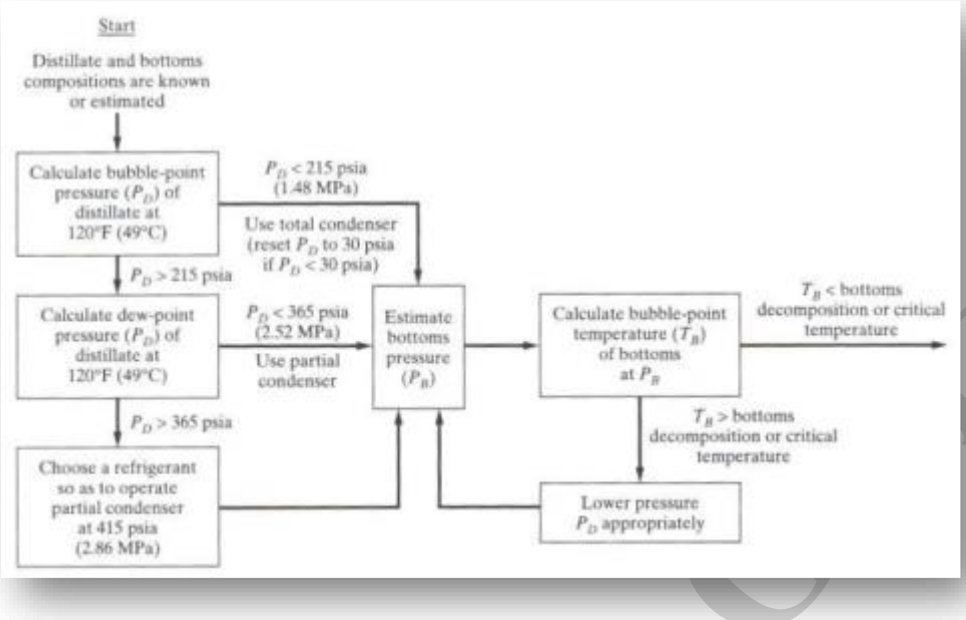

Figure 20 Algorithm for Establishing Distillation Column Pressure and Condenser Type[23]

Since the distillate composition is specified as 99.97% pure methanol, Aspen HYSYS™ can be utilized to estimate the bubble point pressure of this stream at 120°F. A temperature of 120°F is used to estimate the temperature of the distillate because of minimum approach temperature heuristics for cooling water specified by Seider. Aspen HYSYS™ determined the bubble point of this mixture to be 6.8 psia which is below 215 psia; therefore, according to the algorithm in Figure 20 a total condenser is used. In order to avoid vacuum distillation, the total condenser pressure is set to 30 psia. Next, from Seider's method for determining bottoms pressure, 10 psia is added to the condenser pressure to determine the re-boiler pressure which is approximately 40 psia. Finally, Aspen HYSYS™ is used to approximate the bottoms temperature at a pressure of 40 psia to ensure that the bottoms product is below any critical temperatures.

With condenser and re-boiler pressures known, a short-cut distillation column in Aspen HYSYS™ is used to estimate the compositions of the distillate and bottoms streams. The Aspen ComThermo™ package is then used to determine k-values for methanol and water at their distillate and bottoms compositions. The short-cut distillation column in Aspen HYSYS™ can also calculate k-values for estimated compositions and pressures. A summary of compositions, flow rates, temperatures, and pressures associated with all streams related to the distillation column can be found in Table 29.

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[23] Seider Figure 8.9 (pg. 216)

Table 29 Summary of Distillation Streams

Stream	Temperature (°C)	Pressure (kPa)	Flow Rate (Kmole/hr)	Methanol Comp. (Mole Frac.)	Water Comp. (Mole Frac.)	CO Comp. (Mole Frac.)
Feed	50	304	633.9	0.9636	0.0363	0.0001
Distillate	80	206.8	610.9	0.9997	0.0002	0.0001
Bottoms	130.4	275.8	23.08	0.0082	.9918	0

Tray Calculations

Once pressure, composition, and k-values are estimated for all streams associated with the distillation column, the Fenske equation is used to estimate the minimum number of trays (N_{min}) and minimum reflux ratio (R_{min}):

$$N_{min} = \frac{ln\left[\left(\frac{d_{lk}}{b_{lk}}\right)\left(\frac{b_{hk}}{d_{hk}}\right)\right]}{ln\left(\alpha_{lk/hk}\right)}$$

$$\sum_{i=1}^{n} \frac{(\alpha_i)(x_{F,i})}{(\alpha_i - \theta)} = 1 - q$$

$$R_{min} + 1 = \sum_{i=1}^{n} \frac{(\alpha_i)(x_{d,i})}{(\alpha_i - \theta)}$$

After R_{min} and N_{min} are determined, the actual number of stages (N) and the ratio of stages below the condenser to stages above the re-boiler (N_b/N_d) are calculated via the Gilliland correlation and Kirkbride equation respectively.

$$\frac{N - N_{min}}{N + 1} = 0.75\left[1 - \left(\frac{R - R_{min}}{R + 1}\right)^{0.556}\right]$$

$$ln\left(\frac{N_B}{N_D}\right) = 0.206ln\left[\left({}^{B}/_{D}\right)\left(\frac{x_{hk}}{x_{lk}}\right)_F \left[{}^{(x_{lk})_B}/_{(x_{hk})_D}\right]^2\right]$$

Table 30 provides a tray summary for the distillation column that achieves the necessary separations for this process.

Table 30 Tray Summary for Methanol Distillation Column

Column	Total Trays	N_b	N_d	Optimum Feed Stage
Methanol Distillation	16	7	9	7

Tower Diameter and Height Estimation

Once the column is completely specified from previous calculations, the distillation column can be simulated using a full distillation column in Aspen HYSYS™. The resulting simulation is used to obtain important column flow rates and properties such as: vapor flow rate, liquid flow rate, pressure, vapor density, liquid density, and surface tension.

In a fall 2010 Chemical Process Design lecture at the University of Colorado, Dr. Weimer noted that valve type trays for distillation offered a wide flexibility of operating conditions in the distillation process (33). Valve type stainless steel trays were chosen for this process due to their flexibility as Dr. Weimer described in his lecture. Flexibility will be advantageous during the start-up of this process and will allow for a wide range of flows from the upstream reactions while the process is in the start-up phase. Knowing the type of tray is important for determining the capacity parameter from Seider equation 19.13:

$$C = C_{SB} F_{ST} F_F F_{HA}$$

$$F_{ST} = \left(\frac{\sigma}{20}\right)^{0.2}$$

Yang et al. notes in their article named "Improving the Efficiency and Capacity of Methanol-Water Distillation Trays" that there is negligible foaming in this type of distillation system (33). Therefore, the foam factor is assumed to be 1. Seider also notes that F_{HA} is 1 for a valve-type tray. For a valve-type tray with negligible foaming, the capacity parameter is determined to be 0.11 m/s. Next, the flow ratio parameter (F_{LG}) is calculated:

$$F_{LG} = \left(\frac{L}{G}\right)\left(\frac{\rho_G}{\rho_L}\right)^{1/2}$$

Since F_{LG} is calculated to be less than 0.1, (A_d/A_T) used in the diameter equation is estimated to be 0.1. A flooding velocity (U_f) is also calculated from the capacity parameter in Seider equation 19.12:

$$U_f = C\left(\frac{\rho_L - \rho_G}{\rho_G}\right)^{1/2}$$

With a flooding velocity of 1.88 m/s, the diameter of the column is determined by Seider equation 19.11:

$$D_T = \left[\frac{4G}{(fU_f)\pi\left[1 - \left(\frac{A_d}{A_T}\right)\rho_G\right]}\right]^{1/2}$$

The diameter of the column is calculated to be 2.73 m. Finally the height of the column is estimated by multiplying the tray spacing (18 in.) by the total number of trays (16) for a total column height of 8.18 m.

Column Pricing

After the dimensions of the distillation column are established, a price for platforms and ladders depending on its dimensions is calculated.

$$Cpl = 361.8(D_i)^{0.73960}(L)^{0.70684}$$

With a diameter of 8.96 ft and a height of 26.82 ft, the price of platforms and ladders are estimated to be $18,737.

With the known operating pressure of 30 psig inside the separation tower, a cylindrical shell wall thickness is calculated that will be able to safely handle the pressure inside the vessel. First however, a design pressure is calculated that is higher than the actual operating pressure that acts as a pre-cautionary safety measure.

$$Pd = exp[0.60608 + 0.91615\, ln(P_0) + 0.0015655\, ln(P_0)^2]$$

With an operating pressure (P_0) of 40 psig, the design pressure (P_d) is calculated to be 54.98 psig. Based on the calculated design pressure, the shell thickness needed to safely operate at the design pressure is estimated based by Seider equation 22.60:

$$tp = \frac{PdD_i}{2SE - 1.2Pd}$$

Where E is the fractional weld efficiency[24] (E = 0.85) and S is maximum allowable stress (S = 15,000 psi for -20-650°F). Using the calculated design pressure and vessel diameter estimate, the required wall thickness (tp) is calculated to be 0.23 inches. Knowing the density of the carbon steel used as the material to base the cost (ρ=0.284 lb/in^3), the weight of the vessel can be approximated by Seider equation 22.59:

$$W = \pi(D_i + tp)(L + 0.8D_i)tp \times \rho$$

The weight of the vessel is calculated to be 9,118 lbs. With the weight (W) of the vessel calculated, the base cost of the vessel is estimated using Seider equation 22.54:

$$Cv = exp[7.0132 + 0.18255\ln(w) + 0.04333\ln(w)^2]$$

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[24] Seider pg.575

The cost of the vessel (C_v) is estimated to be \$215,381 which does not account for the differences in material. To avoid corrosion, the actual flash separator will be constructed out of S.S 316 which can handle a wide range of materials such as water and methanol. The additional cost of materials is accounted by multiplying the base cost by the material factor (F_m)[25]. The total purchase cost of the column without installed trays is then estimated by adding the cost of platforms and ladders to the factored price of the bare vessel.

$$Cost = (Cv \times (Fm\ (S.S\ 316))/(Fm\ (Carbon\ Steel))\ + Cpl)$$

Where Fm (S.S 316) = 1.7 and Fm (Carbon Steel) = 1

The bare module cost of the vessel without installed trays is estimated to be \$383,744. Next, the price of installed trays is added to the bare-module cost of the distillation tower. The costs of trays are estimated by Seider equation 22.66:

$$C_t = N_t F_{nt} F_{tt} F_{tm} C_{bt}$$

$$F_{tm} = 1.401 + 0.0724D$$

$$F_{NT} = \frac{2.25}{1.0414^{NT}}$$

With an F_{TT} of 1.18, the total cost of trays is estimated to be \$100,950. The total cost of trays is then added to the total cost of the bare distillation tower and multiplied by the appropriate inflation factor (556/500) to estimate the total price of the distillation column in 2010. The total price for the purchased distillation column is approximately \$538,980.

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[25] Seider Table 22.26

Pumps

Seider notes in his text book "Product and Process Design Principles" that "the main purpose of a pump is to provide the energy needed to move a liquid from one location to another" (32). The methanol process described for this project identifies three pumps required to increase the energy of certain process streams. The first pump (pump-1) is a stainless steel centrifugal pump used to increase the pressure of a process water stream that eventually reacts inside the solar reactor. Water enters Pump-1 at atmospheric pressure and 25°C flowing at a rate of 101 gpm which discharges into the solar reactor at 35 bar. Pump-1 was modeled in Aspen Plus™ to determine the flow rate and the net annual energy required for the pump. With the known pressure increase needed to pump water into the reactor and a tabulated value for the specific weight of water ($\gamma = 62.4 \text{lb/ft}^3$), a pressure head in ft. is calculated from Munson equation 12.20 (34):

$$h_a = \frac{\Delta P}{\gamma}$$

The pump head calculated in Munson equation 12.20 is coupled with the volumetric flow rate (Q) in gpm to calculate a size factor for the pump which is calculated in Seider equation 12.13:

$$S = Q(h_a)^{0.5}$$

From the size factor, a base cost is estimated from Seider equation 22.14:

$$Cb = exp[9.7171 - 0.6019\, ln(S) + 0.0519\, ln(S)^2]$$

Seider equation 22.14 estimates the base cost of pump-1 to be \$3,843. After the base cost is calculated, the base cost is multiplied by a material factor (F_M) and a pump-type factor (F_T) found in Seider table 22.20 to estimate the total purchase cost in Seider equation 22.15:

$$C_P = F_T F_M C_B$$

The total purchase price for pump-1 is estimated to be \$7,687. After all of the pricing calculations are repeated for the rest of the pumps, they are added and multiplied by the appropriate CE factor (556/500) to account for inflation. The total price of all pumps for this process is estimated to be \$23,992.

In addition to pricing the pumps, it will be necessary to avoid cavitation and therefore ensure the safety of operators and pumping equipment if the plant is decided to be built. In order to avoid potential cavitation, it will be imperative to make sure the net positive suction head available ($NPSH_A$) is greater than the net positive suction head required ($NPSH_R$). $NPSH_A$ is first calculated from knowledge of the vapor pressure of water at the operating temperature and the pump inlet pressure:

$$NPSH_A = P_{inlet} - P^*$$

Aspen HYSYS™ estimated the vapor pressure of water at 25°C entering pump-1 to be 0.46 psia. Furthermore, with the known inlet pressure of 14.7 psia, $NPSH_A$ was determined to be 14.24 psia. Information regarding $NPSH_R$ will be provided by the manufacturer in the form of a pump curve once pieces of equipment are being purchased for the construction of the plant. $NPSH_R$ values are specific for each pump so it must be determined by the pump manufacturer. Once a detailed design of the plant is made, cavitation will be avoided by making sure $NPSH_A$ is greater than $NPSH_R$. If $NPSH_R$ is larger than $NPSH_A$, then several measures can be taken to increase $NPSH_A$ including: decreasing water temperature to decrease P^*, increasing P_{inlet} by storing the pumping water in an elevated tank, or pressurizing the inlet stream with an additional pump at a lower pressure head. Table 31 summarizes flow rates, NPSH, and pricing for all three process pumps.

Table 31 Summary of Design Specifications and Pricing for Process Pumps

Pump	Q (gpm)	Head (ft)	$NPSH_A$ (psia)	$NPSH_R$ (psia)	Price
1	101	1137	14.24	NA	\$8,548
2	655	1137	14.24	NA	\$16,131
3	115.1	67.8	16.42	NA	\$6,830

Heat Exchangers

Heat exchangers are incorporated into the design of this process in order to add and remove heat from the distillation column. Specifically, low pressure steam is used as a heat transfer agent in a shell-and-tube heat exchanger used as a re-boiler for the distillation column. In addition to the re-boiler, another shell-and-tube heat exchanger is used to completely cool and condense the vapor distillate into liquid using cooling water. The method employed for designing and pricing the heat exchangers follows Seider's method described in chapter 18 and chapter 22.

The design of both heat exchangers as described by Seider is based off of temperature driving forces. In the condenser, which is modeled as a shell-and-tube heat exchanger, reasonable temperature estimates are made for all inlet and outlet streams. First, the full distillation column modeled in Aspen HYSYS™ estimates the temperatures of the hot-in and hot-out temperatures for the condenser which are streams To Condenser and MeOH in the simulation respectively. Temperatures for the cold-in and cold-out streams in the re-boiler are also estimated by Aspen HYSYIS™. Example calculations will be shown through the ones performed to design and price the condenser.

The cold-in temperature, which is assumed to be cooling water provided at 90°F, cools the hot-in stream and approaches a minimum approach temperature provided by heuristics. A summary of inlet and outlet streams for both heat exchangers are provided in Table 32.

Table 32 Summary of Cold and Hot Streams in Distillation Condenser and Re-boiler

Heat Exchanger	$T_{Cold\text{-}In}$ (°F)	$T_{Cold\text{-}Out}$ (°F)	$T_{Hot\text{-}In}$ (°F)	$T_{Hot\text{-}Out}$ (°F)
Condenser	90	146	190.1	166
Re-boiler	266.4	266.8	280.4	276.8

Once reasonable temperatures are estimated for all streams, the log-mean temperature difference is calculated with Seider equation 18.3:

$$\Delta T_{LM} = \frac{\Delta T_1 - \Delta T_2}{ln\left(\frac{\Delta T_1}{\Delta T_2}\right)}$$

Next, in order to calculate the correction factor (F_T), R and S factors are calculated via Seider Equation 18.5 and 18.6 respectively:

$$R = \frac{T_{hin} - T_{hout}}{T_{cout} - T_{cin}}$$

$$S = \frac{T_{cout} - T_{cin}}{T_{hin} - T_{cin}}$$

Once R and S are evaluated at their respective process temperatures, the correction factor (F_T) is calculated via Seider equation 18.4:

$$F_T = \frac{\sqrt{R^2+1}\, ln\left[\frac{1-S}{1-RS}\right]}{(R-1)\left[ln\frac{\left[2-S\left(R+1-\sqrt{R^2+1}\right)\right]}{\left[2-S\left(R+1+\sqrt{R^2+1}\right)\right]}\right]}$$

The shell-and-tube heat exchanger factors are summarized in Table 33 for the re-boiler and condenser.

Table 33 Summary of Heat Exchanger Factors for Condenser and Re-boiler

Heat Exchanger	R	S	F_T
Condenser	0.43	0.56	0.93
Re-boiler	9	0.03	1

With appropriate correction factors calculated, the type of heat exchanger is determined from comparing these factors with Seider figures 18.14 and 18.15. Both heat exchangers coincide with figure 18.14, therefore they are designed to be 1-2 shell-and-tube heat exchangers. Next, the true mean temperature driving force (ΔT_m) is calculated from ΔT_{lm} and F_T with the following equation:

$$\Delta T_m = F_T \Delta T_{lm}$$

Once the true mean temperature driving force is estimated, the total outer surface area of tubes is estimated from the net duty of the heat exchanger simulated in Aspen HYSYS™ and a reasonable estimate for the overall heat-transfer coefficient (U).

$$Q = UA\Delta T_m$$

Seider table 18.5 provides sensible heat transfer coefficients for low boiling hydrocarbons and water which is used to estimate the surface area in both heat exchangers. Table 34 provides a summary of heat duty, overall heat transfer coefficient, mean-driving force temperature, and a surface area estimate for both heat exchangers.

Table 34 Summary of Key Design Features for Condenser and Re-boiler

Heat Exchanger	Duty (BTU/hr)	U (BTU/ (°F-Ft^2-hr))	ΔT_m (°F)	A (ft^2)
Condenser	3.09E7	140	54.5	4,044
Re-boiler	3.29E7	140	11.9	19,740

Seider estimates the base price of shell-and-tube heat exchangers based on their overall heat transfer surface area (A) in Seider equation 22.41:

$$C_B = exp[11.0545 - 0.9228\, ln(A) + 0.09790\, ln(A)^2]$$

According to Seider, the base price for the condenser and re-boiler are $28,871 and $113,353 respectively. Next, the purchase price of the heat exchangers is estimated by multiplying the base price by a material factor, length factor, and an inflation factor (556/500). The material factor is calculated via Seider equation 22.44:

$$F_m = a + \left(\frac{A}{100}\right)^b$$

Where a and b are constants given in Seider table 22.25 for a stainless steel/stainless steel heat exchanger. The purchase price for the condenser and re-boiler both constructed out of stainless steel in 2010 is estimated to be $121,127 and $493,661 respectively.

IX. Utility Summary

The utilities required in the former described process are electricity, cooling water, and low pressure steam (LPS) which are assumed to be available at the price of \$0.06/kW-h, \$0.019 m^3, and \$7.86/1000kg respectively. In the biomass to methanol process, electricity is required to power all pumps, the compression system, and the fired pyrolysis furnace. Cooling water, as the name suggests, is used to cool the following unit operations: compressor, methanol reactor, and the distillation condenser. Cooling water is also required to react in the solar reactor and to quench the resulting effluent gas in the spray quench tank. LPS is utilized as the heat transfer agent in the re-boiler system located at the bottom of the distillation column. All duties for these unit operations are simulated by Aspen HYSYS™ and Aspen Plus™. Cooling water requirements are also taken from values simulated by Aspen HYSYS™ and Aspen Plus™.

Electrical utilities are priced based on their net power duties required to power electrical equipment. Therefore the hourly utility cost for pump-1 requiring 40.11 kW is priced in the example calculation below:

$$Hourly\ Pump-1\ Utility\ Cost = 40.11\frac{kW}{kW-hr}\left(\frac{\$0.06}{kW-hr}\right) = \frac{\$2.41}{hr}$$

Since pump-1 runs 8 hours per day for a total of 365 days per year, the total cost/year is calculated below:

$$Annual\ Electrical\ Utility\ Cost = \left(\frac{\$2.41}{hr}\right)\left(\frac{8hr}{day}\right)\left(\frac{365day}{yr}\right) = \$7{,}027.27/year$$

A summary of electrical utilities can be seen in Table 35 for all unit operations requiring electricity.

Table 35 Summary of Electrical Utilities Provided to Production Facility

Equipment	Required Duty (kW)	Annual Duty (kW-hr)	Cost/kW-hr (USD)	Annual Cost (USD)	Cost/gal MeOH (USD/gal)
Pump-1	40.11	117121.2	0.06	7,027.272	0.000125
Pump-2	190.56	556435.2	0.06	33,386.11	0.000596
Compressor	15642	45674640	0.06	2,740,478	0.048937
Fired Heater	1103	9662280	0.06	579,736.8	0.10352
Pump-3	1.9	16644	0.06	998.64	1.78E-05
Total	16977.57	56027120.4	-	3,361,627	0.060029

In a similar fashion, the price for cooling water utilities into the spray quench tank can be calculated from cooling water flow rates input into Aspen Plus™. A sample calculation for determining the utility cost for the cooling water required to achieve 100% conversion in the solar reactor is performed below:

$$Annual\ H_2O\ Utility\ Cost = \left(\frac{148.73m^3}{hr}\right)\left(\frac{8hr}{day}\right)\left(\frac{365\ day}{year}\right)\left(\frac{\$0.019}{m^3}\right) = \$8{,}251.54/year$$

The amount of cooling water required to condense the distillate in the distillation condenser is determined through an enthalpy balance on cooling water. Cooling water is assumed to be a saturated liquid at a temperature of 90°F. The cooling water cools the resulting distillate stream at a 20°F approach temperature which is calculated in the heat exchanger design of the condenser. The properties of saturated cooling water at the approach temperature (63.3°C) are determined using saturated steam tables. The mass flow rate (m) of water is determined via the following equation:

$$Q = m\Delta H = m(H_{out} - H_{in})$$

Based on the condenser duty (Q) of 3.25E7 kJ/hr, the mass flow rate of condenser cooling water is determined to be 5.05E5 Kg/hr (See Appendix D for detailed calculation). The volume of water required to condense the distillate stream is then evaluated from its specific volume at the inlet temperature. Once the flow rate of water is known, the price of the utility is determined from the previous cooling water utility price equation. A summary of cooling utilities required for the process can be seen in Table 36.

Table 36 Summary of Cooling Water Utilities Provided to the Production Facility

Equipment	Required Duty (m^3/hr)	Annual Duty (m^3)	Cost/m^3 (USD)	Annual Cost (USD)	Cost/gal Methanol (USD/gal)
Solar Reactor	22.7628	66467.376	0.19	12,628.8	0.000226
Spray-Q-T	148.73	434291.6	0.019	8,251.54	0.0001473
Interstage Cooler	17.74623	51818.97802	0.019	984.56	0.0000176
Methanol Reactor	17.1109	49963.83647	0.019	949.31	0.000017
Condenser	5.05E+02	4.43+06	0.019	8.41E4	0.0015022
Total	711.79	5030224.53	-	106,940.20	0.00191

Similar to the cooling water utilities required for heat transfer, the LPS utility to the re-boiler is also determined via an enthalpy balance on the system. LPS steam is assumed to be a saturated vapor at 50 psig and 147°C. The steam flowing inside of the re-boiler is assumed to be condensing which delivers its heat of vaporization to the vaporizing liquid. The resulting outlet low pressure stream utility is evaluated in steam tables at the saturated outlet temperature which was determined in the heat exchanger design of the re-boiler. Once the properties of saturated water at the inlet and outlet conditions are determined, the mass flow rate of LPS is calculated from a simple enthalpy balance on the re-boiler. The duty (Q) of the re-boiler is simulated in Aspen HYSYS™ and used to calculate the mass flow rate (m) of LPS in the equation below:

$$Q = m\Delta H = m(H_{in} + H_{vap} - H_{out})$$

For a net duty of 3.47E7 kJ/hr, LPS steam must be fed at a rate of 8,055.49 Kg/hr (see Appendix D for detailed calculations). The price of this utility is estimated from the assumption that LPS is provided at $7.86/1000kg in the equation below:

$$Annual\ LPS\ Utility\ Cost = \left(\frac{9{,}261kg}{hr}\right)\left(\frac{8000hr}{year}\right)\left(\frac{\$7.86}{1000kg}\right) = \$637{,}719.70$$

A summary of LPS utilities are summarized in Table 37.

Table 37 Summary of Low Pressure Steam Provided to Production Facility

Equipment	Required Duty (kg/hr)	Annual Duty (kg/year)	Cost/kg (USD)	Annual Cost (USD)	Cost/gal Methanol (USD/gal)
Re-boiler	8055.498	70566158.56	0.00786	554,650	0.009904
Total	8055.498	70566158.56	-	554,650	0.009904

X. Estimation of Capital Investment & Total Product Cost

Estimation of Capital Investment and Selling Methanol Selling Price

In order to estimate the total capital investment (TCI) required for producing 56 million gallons of fuel-grade methanol (99.97%) per year; a case study was conducted based on the price of major equipment required to complete the specifications. Calculations used to estimate TCI are performed in a Microsoft excel spreadsheet written by Miles Julian, a former business consultant for DuPont. The goal of this economics spreadsheet is to provide an estimate of TCI within 30% of its actual value.

First, the direct installed cost (DIC) is calculated for the pieces of equipment for which only the delivered equipment cost (DEC) is known. The economics spreadsheet provided by Dr. Weimer estimates miscellaneous equipment to cost 10% of the DEC, giving the DEC a value of $43.093 MM. Field maintenance, labor, and insulation are estimated to cost 5%, 10%, and 10% of the DEC, respectively. In addition to the previous assumptions, foundations, supports, and platforms are estimated to cost 10% of the DEC. The sum of these expenses comes to a total of $66.247 MM. Next, the cost of integrating purchased pieces of equipment into the process are accounted for by assuming the price of piping, process control instruments, and electrical wiring are 22%, 9%, and 7% of the installed equipment cost, respectively. The addition of these process integration expenses extends the subtotal DIC cost to $91.421 MM. Based on this subtotal, freight, quality assurance, sales taxes, and overhead expenses are factored into the subtotal using a 60% material percentage in labor/material split. Furthermore, contractor labor costs are estimated to be 44% of the split labor portion. These assumptions on freight, quality assurance, sales tax, and overhead expenses bring the DIC subtotal to $114.093 MM. Additional indirect costs are estimated to be 15% of this subtotal; therefore bringing the total DIC for pieces of equipment initially priced with the DEC to $131.207 MM.

The price of heliostats, secondary concentrators, distillation column, tower, solar reactor, methanol reactor, and carbide tubes include direct installation so they are considered to be equipment at the bare module level with a bare module factor (F_{BM}) of 1. 10% is added to the price of equipment that included direct installation to account for any miscellaneous equipment needed. The total of all direct installed costs including the ones estimated from DEC come to $217.082 MM.

The total permanent investment (TPI) includes the costs of structures and start-up. The cost of buildings is assumed to be 5% of the DIC which was provided by Dr. Weimer in an e-mail on 12/20/2010. A typical percentage of building costs on total investment is 20%; however, since the solar equipment does not require a building the factor for this process is much lower, say 5%. The total direct installed cost of equipment with the price of additional buildings and structures is estimated to be $227.936 MM. Power, dismantling, rearranging, and site development are estimated to 2%, 2%, and 4%, respectively. Accounting for these factors brings the subtotal to $246.171 MM. Unexpected costs, or contingency, are accounted into the total cost by assuming it is 15% of the previous total, resulting in a total equipment cost of $283.097 MM. A site factor of 0.95 for the US Southwest was also incorporated into the cost which was provided in the same e-mail by Dr. Weimer discussed previously. In addition to the site factor, a 1.9% inflation rate for two years results in a grand total TPI of $294.000 MM.

Along with TPI, working capital (WC) is estimated and added to the investment in order to cover costs for early plant operation. Working capital is estimated by determining the raw materials needed for the first three months of start-up. The amount of biomass, methane, and water needed for the first 90 days can be calculated using the mass flow rates required for operation. Since the methanol reactor catalyst is only required once over the entire 15 year life of the plant, the total cost of this catalyst is incorporated into the working capital. Since the zinc oxide catalyst needs to be replaced every three years during the plant's lifetime, only the cost of zinc oxide for three years is integrated into the working capital. Methanol catalyst is by far the most dominant cost, accounting for close to 99% of the entire raw materials inventory costs. In addition to raw materials, about $7.4MM will be added to the total working capital which accounts for the need of spare parts during start-up. Therefore, the total working capital for the plant is estimated to be $31.582 MM which is close to 10.8% of the total permanent investment.

Variable and Fixed Costs

Variable costs include: ingredients, utilities, and catalysts. Biomass, methane, zinc oxide, and feed water are considered to be the ingredients for producing pure methanol. The amount of key ingredients required to produce one gallon of pure methanol is calculated by taking the amount of each key ingredient used in its characteristic unit per year and dividing it by 56 million gallons of pure methanol made per year. The following table summarizes the units of ingredient required for producing one gallon of methanol.

Table 38 Summary of key ingredients used in producing methanol

Ingredient	Unit of Measure	Units consumed/ year	Cost per Unit (USD/unit)	Unit/gal MeOH
Methane	SCF	5,880,000,000	.004	35
Biomass	Metric Ton	208,128	60	0.0012
Process Water	M^3	182,080	0.19	0.00108

The ingredients used in the gasification of biomass process have the following costs: biomass is $60.00/metric ton, methane is $.004/SCF, and process water is $0.19/m^3. These costs give a total ingredient cost of $0.215 per gallon of pure methanol produced.

Low pressure steam (150 psig), electricity, cooling water, and solid waste disposal are considered to be utilities required for the production of fuel-grade methanol. The amount each utility required per gallon of pure methanol produced is calculated via the same way key ingredients are accounted for. Table 39 shows a summary of utilities related to methanol production. Utilities account for $0.107 of costs for producing one gallon of fuel-grade methanol.

Table 39 Summary of utilities

Utility	Units	Cost per Unit (USD/unit)	Unit of Utility/ gallon MeOH
150 psig steam	kg	0.00786	1.15
Electricity	kW-hr	0.06	0.914
Cooling water	M^3	0.019	0.081
Waste Treatment	kg	0.31	0.134

In addition to key ingredients, ZnO is the only catalyst that needs to be accounted for in catalyst costs. Methanol catalyst was already accounted for in working capital, so the only catalyst accounted for in variable costs is ZnO. The current cost of catalyst is assumed to be $0.20/kg. The cost of catalyst per gallon of pure methanol was calculated knowing the amount of catalyst needed over the last 12 years of operation since enough ZnO catalyst was covered in working capital for the first three years of the plant's life.

The amount of catalyst needed for 12 years was then divided by the amount of methanol produced in 12 years to get the amount of catalyst per gallon of pure methanol. The amount of catalyst required per gallon of methanol is 0.032 kg/gal, bringing the price of catalyst per gallon of methanol to $0.328/gal. A byproduct credit is supplied by both the federal and state government at $0.40/gal to help offset the cost of research, development and production. Therefore, the total variable cost including the price of ingredients, utilities, catalyst and byproduct credit is $-4.041MM per year. The negative sign here indicates a total net profit.

Operator Costs

The human cost of running this plant must also be considered. To do this, we divide the plant into the major steps required to run the process. Upstream, we have the solar reactor, the Zinc Oxide reactor and the methanol reactor, all of which are run in semi-batch mode due to the sun powering the solar reactor. Downstream we have the raw methanol distillation section which runs continuously.

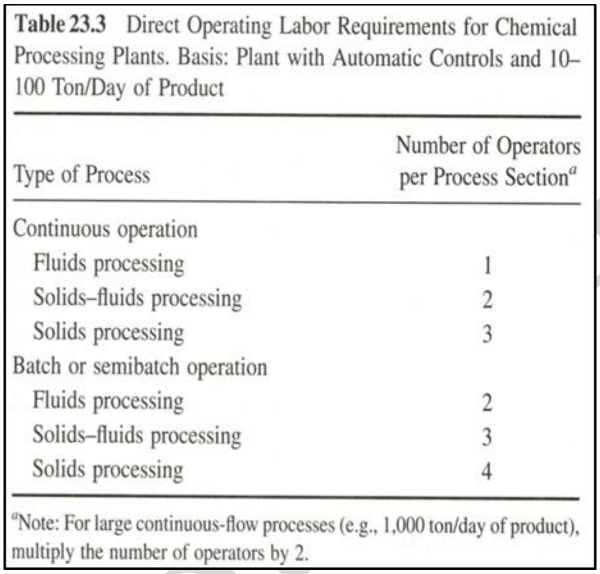

Table 23.3 Direct Operating Labor Requirements for Chemical Processing Plants. Basis: Plant with Automatic Controls and 10–100 Ton/Day of Product

Type of Process	Number of Operators per Process Section[a]
Continuous operation	
Fluids processing	1
Solids–fluids processing	2
Solids processing	3
Batch or semibatch operation	
Fluids processing	2
Solids–fluids processing	3
Solids processing	4

[a]Note: For large continuous-flow processes (e.g., 1,000 ton/day of product), multiply the number of operators by 2.

The solar reactor and Zinc Oxide reactor both require solids and fluids processing and are staffed by three operators each on any given shift. The Methanol reactor is a fluids based process and requires two operators. Downstream separations are continuous, and count as large scale. They are therefore staffed by 2 operators.

In a typical work week, people work 40 hours each. There are 168 shift hours which must be covered, or roughly 4.2 shifts. In order to account things like sick days, vacation etc., 5 shifts per operator is planned for rather than 4.2. In total, roughly 50 operators are required to run the process. We assume that each operator is paid $104,000 per year including all insurance and benefits (32).

XI. Profitability Analysis

The plant lifetime for the solar gasification of biomass to methanol process described in this case study is expected to operate for 15 years with an additional year for construction. Cash flow can be seen as a function of years in the following figure.

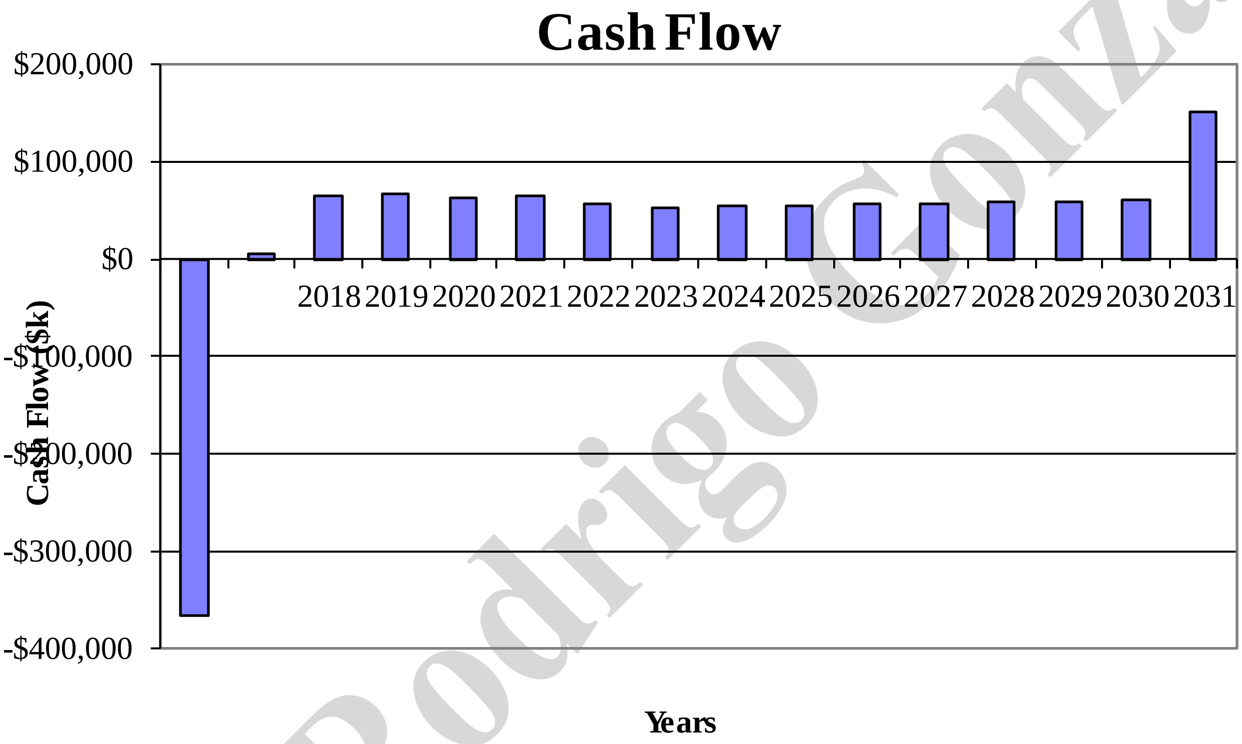

Figure 21 Cash flow projection over lifetime of methanol plant

During the first year of the plant's life, cash flow is negative representing the costs for design, construction, and working capital required to build the plant, before any production begins. In 2011, however, the cash flow becomes positive. This trend represents start up and optimization of the plant as unanticipated problems are solved during the first start-up year and the full methanol capacity being reached. An acceleration of cash flow is observed after the first year followed by a decrease and leveling off. Cash flow is calculated based on Modified Accelerated Cost Recovery Depreciation (MACRS) with a class life of five years which accounts for this observed trend. During the final year, cash flow spikes above any other year, representing liquidation of the plant as pieces of equipment are sold off and salvaged.

In order to achieve an investor's rate of return (IRR) of 12.5%, the economics spreadsheet calculates the selling price of methanol to be \$1.56/gal. Net present value "(NPV) is the difference between the present value of the annual cash flows and the initial required investment". Therefore, for an IRR of 12.5%, the NPV is \$202.718 MM at the end of each period.

For a selling price of \$1.56/gal methanol, the return on investment (%ROI) is expected to be 13.2% over the 16 year plant life. ROI is a measurement of a plant's profitability which is the ratio of net earnings to total capital investment.

$$\%ROI = \frac{Net\ Earnings}{TCI}$$

Payback period (PBP) for this plant is defined as the time required for recovery of the TCI. The total capital investment for this plant is expected to be recovered within 7.6 years. PBP is defined in the following equation:

$$PBP = \frac{Depreciable\ Capital}{Cash\ Flow}$$

Depreciable capital is measured in the spreadsheet through straight-line depreciation which offers a rough estimate of the actual rate of depreciation. Though PBP and %ROI are crude profitability estimates, they offer important insight into whether the investment should be made or not.

IRR has a significant effect on selling price of methanol, ROI, PBP, and NPV. A summary of the effect IRR has on these variables can be seen in the following table.

Table 40 Effect of %IRR on methanol selling price, %ROI, PBP, and NPV

%IRR	Selling Price methanol ($/gal)	%ROI	PBP (years)	NPV ($k at end of period)
1	.74	5.1	19.5	68,890
5	.98	7.5	13.3	10,819
10	1.35	11.2	9.0	132,619
12.5	1.56	13.2	7.6	202,718
15	1.78	15.4	6.5	278,762
20	2.29	20.3	4.9	447,750
25	2.86	25.5	3.9	637,400

Sensitivity Analysis

A multitude of factors affect the target selling cost of methanol and can in the end make or break the entire project should any one of them change significantly from the original assumptions presented. The single largest factor that determines the profitability of a project is the Total Principle Investment (TPI). Figure 1 below shows the decreasing non-linear relationship between ROI and IRR as TPI increases.

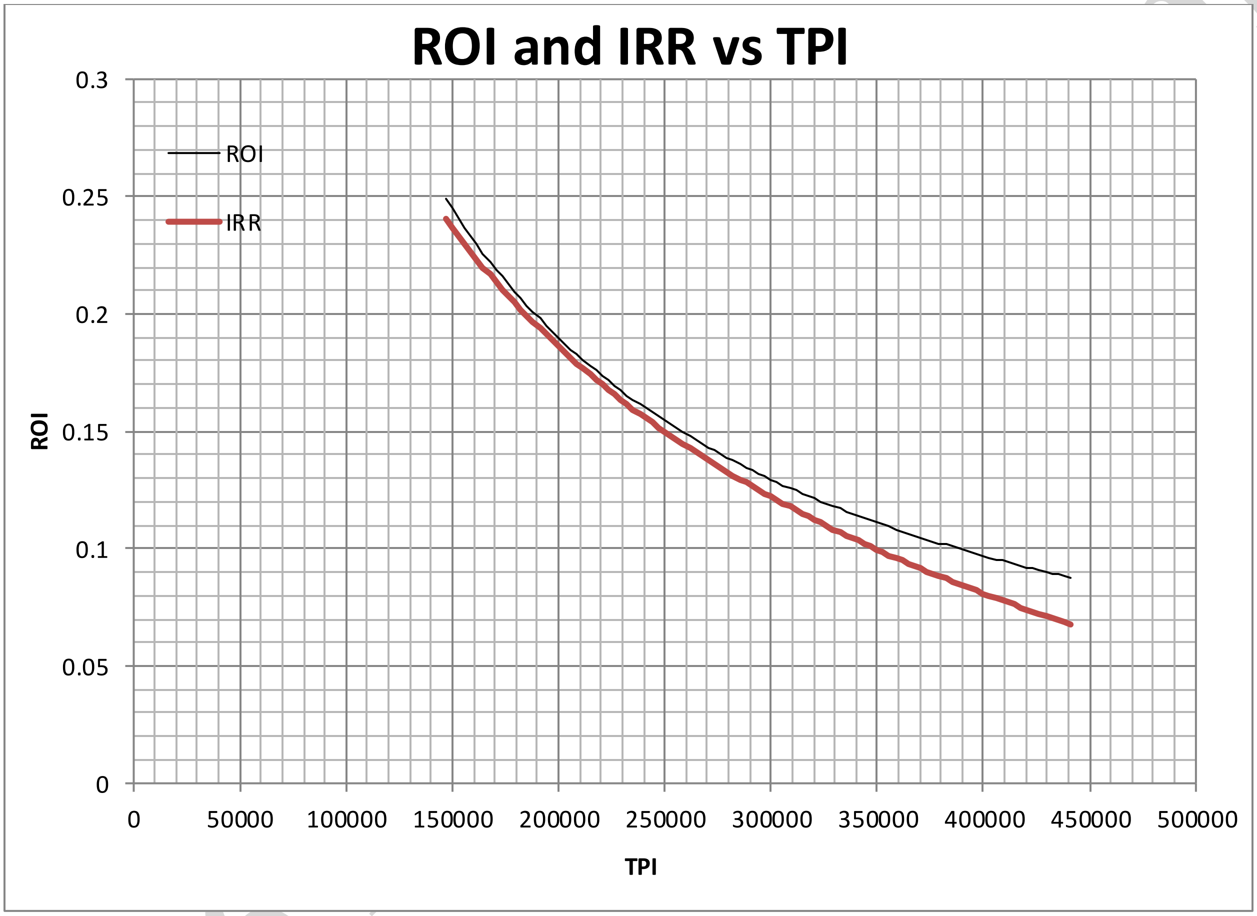

Figure 22 Sensitivity plot of a 50% change in TPI and its effects on ROI and IRR (shown in dark red and blue respectively)

The largest factor in our process which contributes to TPI is the cost of the heliostat. As can be seen in the figure below, the cost of the heliostat has a very similar effect as that of TPI.

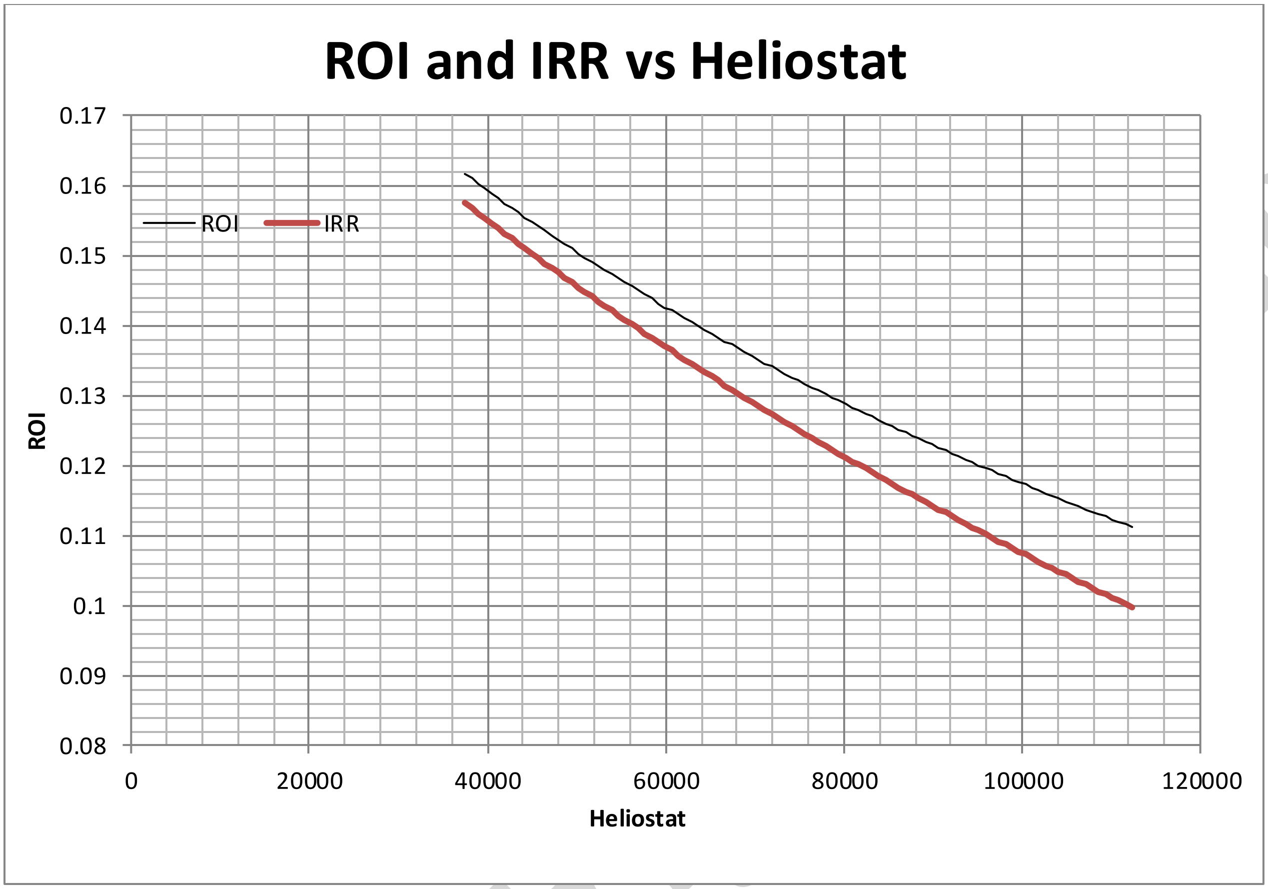

Figure 23 Sensitivity plot of a 50% change in Heliostat Cost and its effects on ROI and IRR (shown in dark red and blue respectively)

The figures below show how increasing costs of raw materials directly decreases IRR and ROI

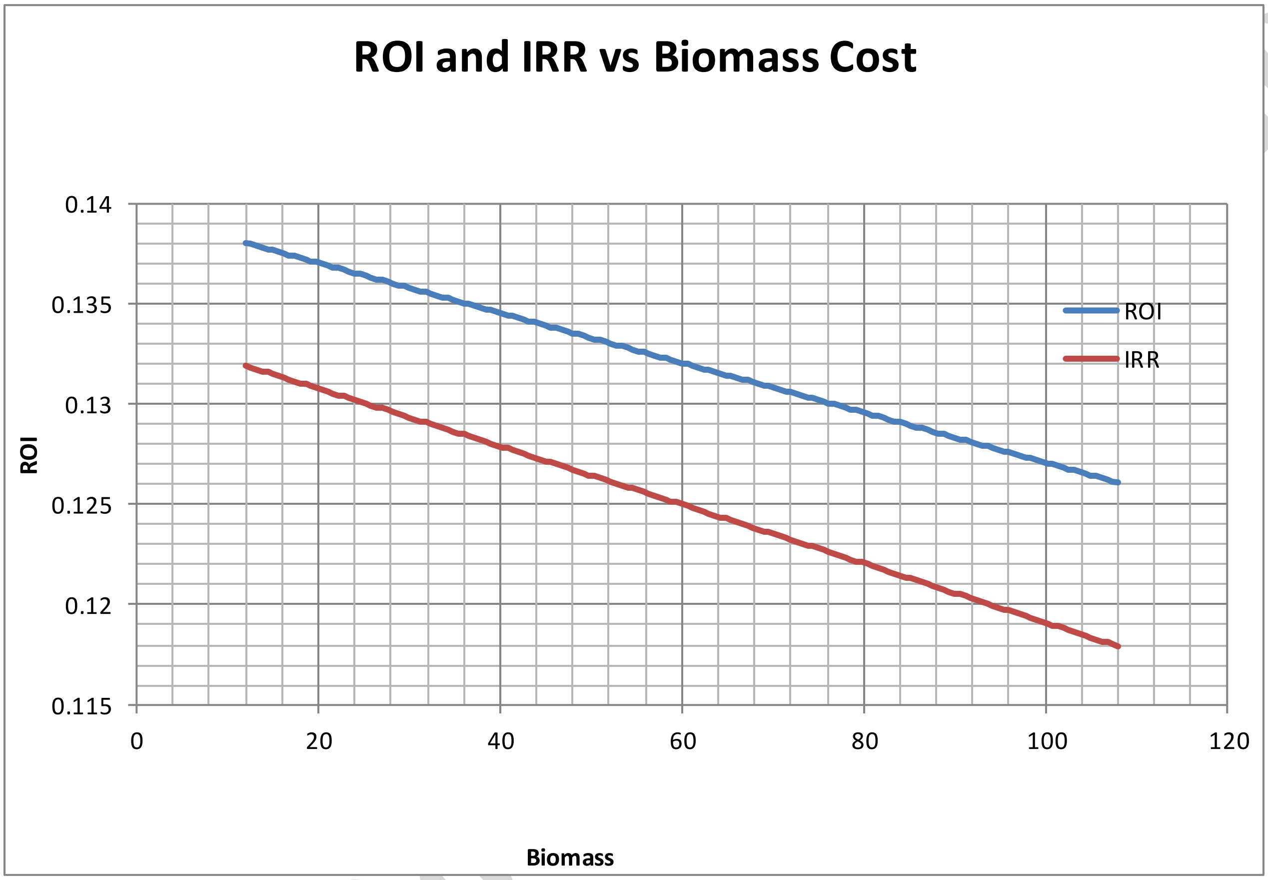

Figure 24 Sensitivity plot of an 80% change in Biomass Cost and its effects on ROI and IRR (shown in dark red and blue respectively)

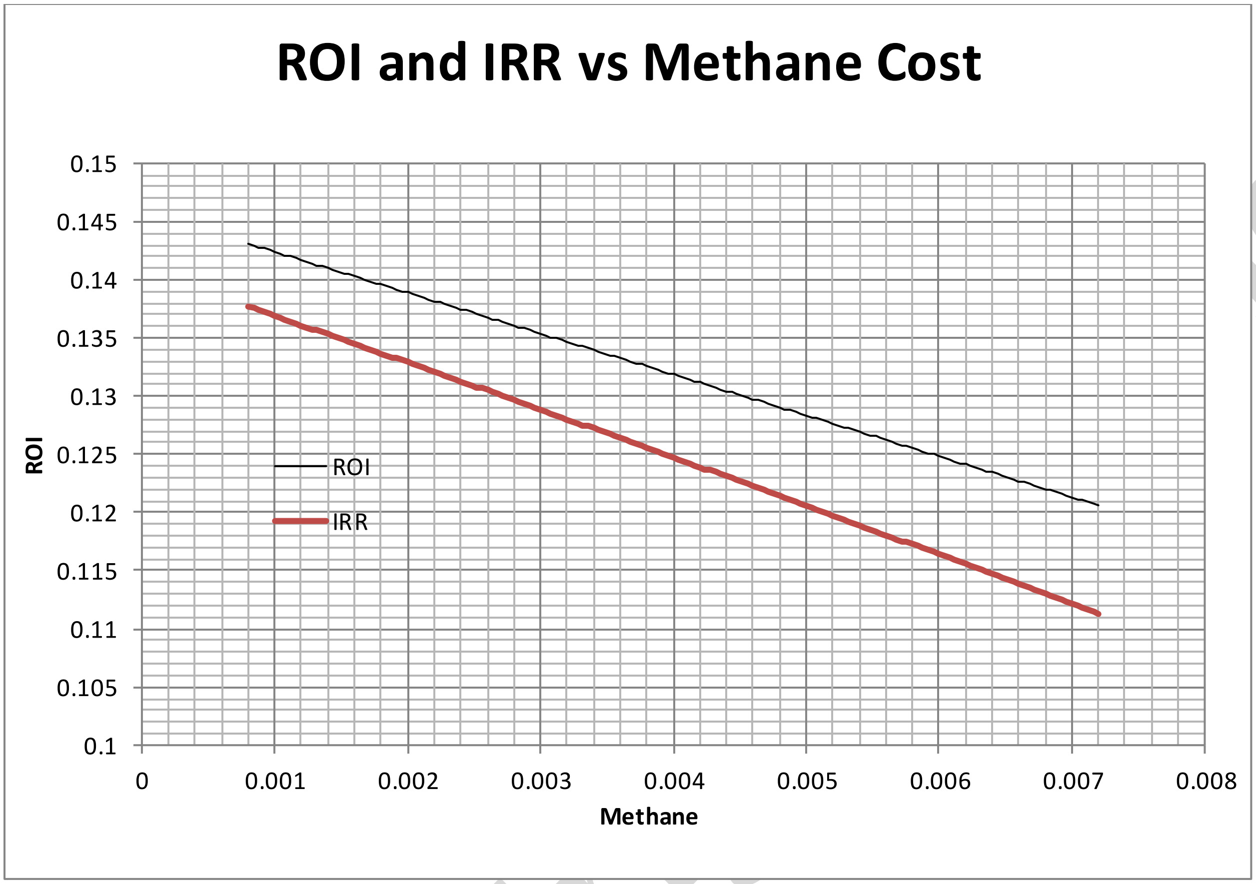

Figure 25 Sensitivity plot of an 80% change in Methane Cost and its effects on ROI and IRR (shown in dark blue and red respectively)

Desired rate of return also directly affects the price at which methanol must be sold. As we can see below, higher rates of return non-linearly increase the price which methanol must be sold.

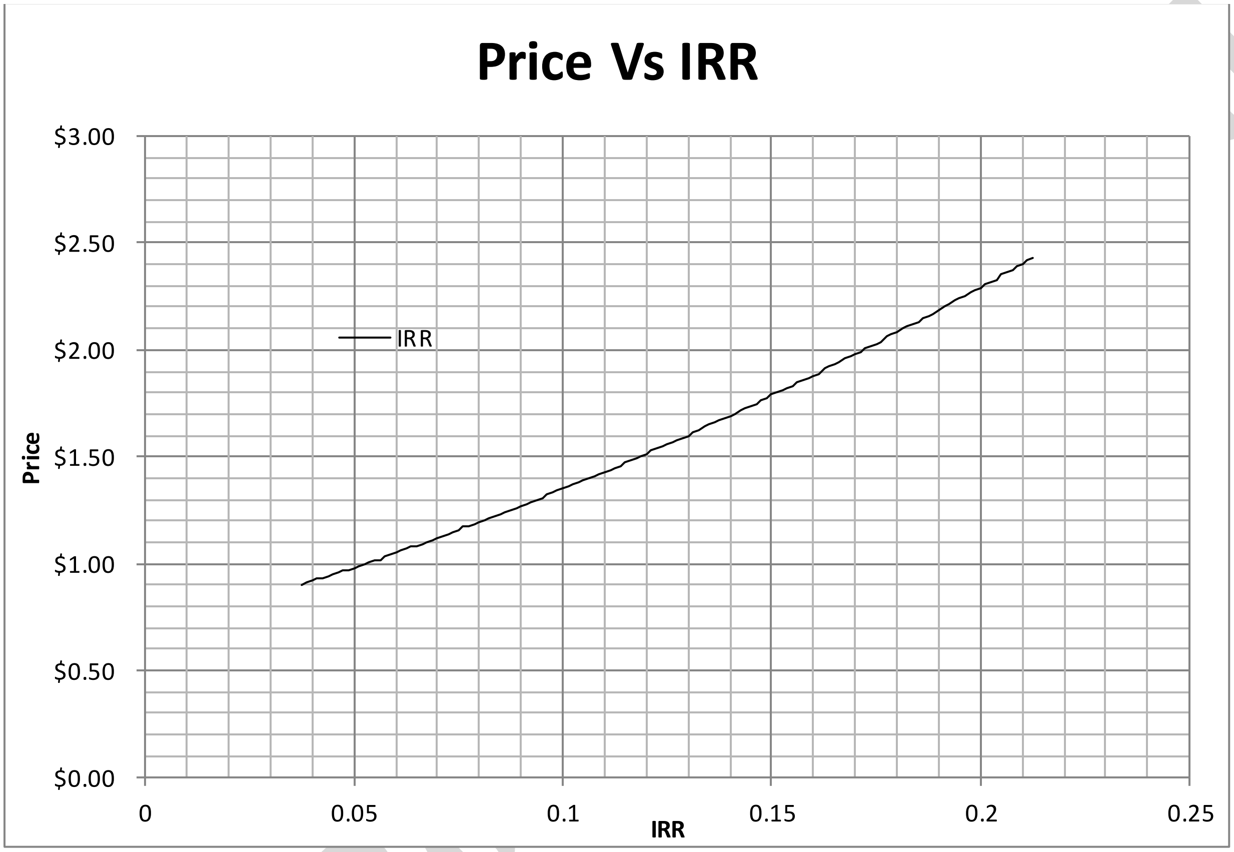

Figure 26 Sensitivity plot of changes in the selling price of methanol as IRR increases

Methanol production via our route is not currently viable economically, despite government subsidies. The figure below shows how that methanol must be subsidized at roughly $0.9/gal as opposed to $0.4/gal as it is currently for this process to be economically viable.

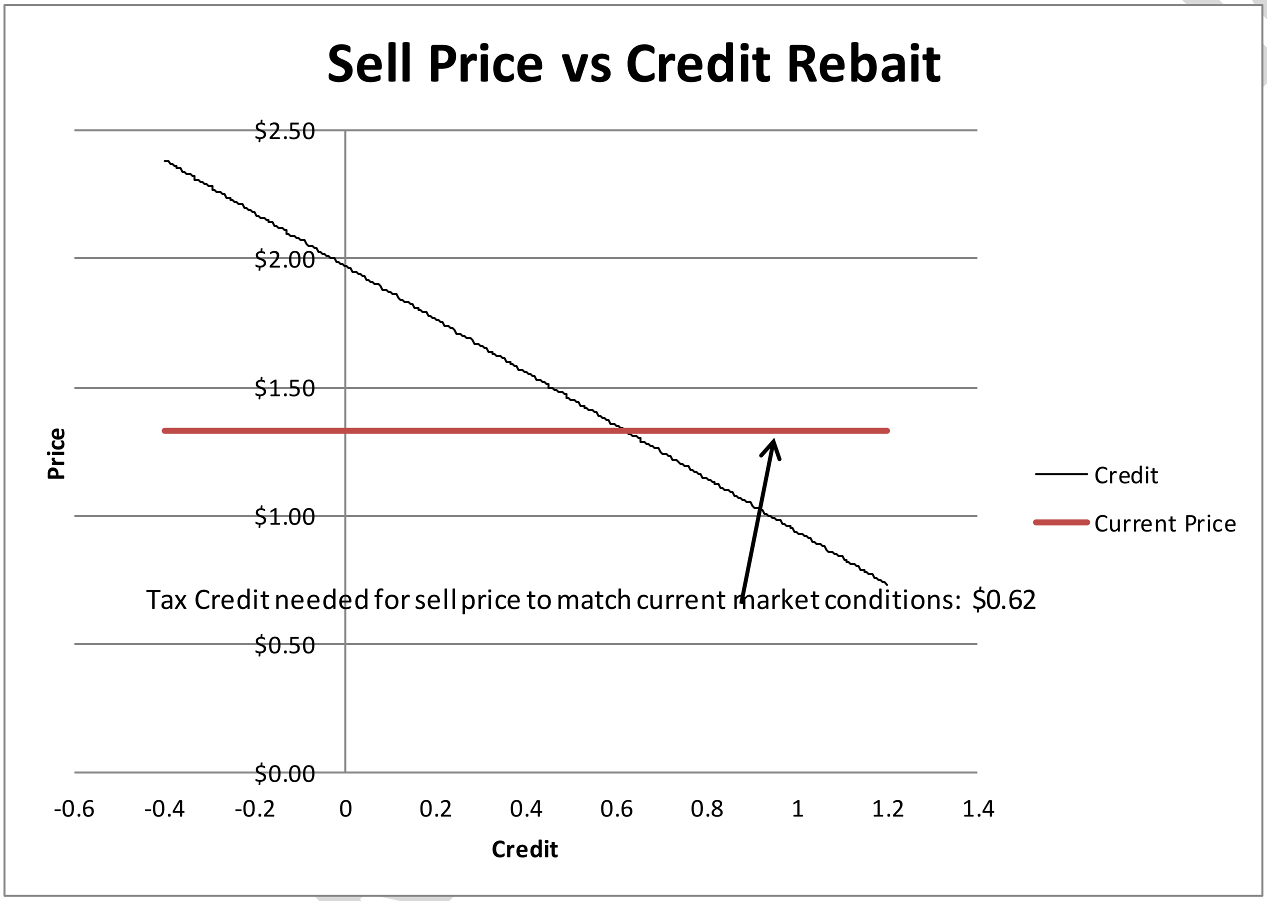

Figure 27 Sensitivity plot of changes in the selling price of methanol as subsidies increase

XII. Conclusion

Solar conversion of biomass to fuel-grade methanol is a clever technique that may have a potential to fuel our world in the future. However, at this current point in time, this process is not an economically feasible option for producing fungible fuels such as methanol. At a 12.5% IRR and an estimated total capital investment of $204.6MM the estimated selling price of methanol is $1.88/gal compared to competitors whom can reduce costs enough to sell methanol at $1.30/gal. In order to reduce the price of methanol and therefore make it competitive, a selling price of $1.30/gal would result in a 0.1% IRR and 5.8%ROI within a long 17.3 year payback period. With such low returns on investment, this process would not receive interest from potential investors looking to finance the project.

Though the model of this plant does not suggest profitable margins, there might be several ways that this process can become profitable in the future. Government programs that provide tax credits to new emerging "green technologies" and companies might be a plausible way that the selling price of methanol can be subsidized enough to become competitive with less "green" processes. Furthermore, the process modeled in this case study could have taken further measures to reduce energy consumption and overall costs. The compressor system in the upstream process was estimated to consume approximately 3 million dollars' worth of electricity per year. In hindsight, a turbine could be added after the methanol reactor to recover some of the energy lost in this high pressure stream. With a 70% efficient turbine system, electrical utilities for the compressor system could potentially decrease to 1 million dollars per year. In addition to an added turbine, exploring the possibility of regenerating ZnO absorbent in the ZnO bed reactor could drastically reduce costs. In this modeled process, ZnO, a relatively expensive absorbent is thrown away every 3 years. Throwing away the absorbent requires fresh ZnO to be purchased every 3 years at an approximate cost of 24 million dollars over the 15 year operating period of the plant. Regenerating even a fraction of the ZnO absorbent will decrease costs and therefore increase the profitability of this process. Since the total capital investment is dominated by the price of the heliostat field which is a relatively new method of harvesting solar energy; this process could potentially become profitable if the fields drop in price overtime as they increase in efficiency and decrease in purchase costs. Furthermore, as the public becomes more aware and concerned about environmental responsibility; government subsidies mentioned before could drive the price of heliostat solar harvesting down to a price that is profitable.

Though there are possibilities that could potentially make this process profitable in time to come, the realistic answer is that it will not become economical in the short future. In the current economy, there is not enough funding from investors to supply a project that will not be cost-competitive and profitable.

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Appendix A. Approach Calculations

Heats of Reaction

$$\Delta H_r^\circ = \sum_{reac\tan ts} |v_i|(\Delta H_c^\circ)_i - \sum_{products} |v_i|(\Delta H_c^\circ)_i$$

To calculate the heats of reaction use Hess's Law*
where vi is the stoichiometric coefficient of species I, and Delta Hc is the heat of combustion

*Equation obtained from Felder and Rousseau (2005)

Heat of Reaction of Dry Cellulose and Steam

Dry Cellulose (25 C)

$$C_6H_{10}O_{5(s)} + H_2O_{(g)} \longrightarrow 6CO_{(g)} + 6H_{2(g)}$$

Species	Stoichiometric Coefficient	ΔH combustion		State
Dry cellulose	1	-17340 J/g[‡]	-2811.51 kJ/mol	solid
Water	1		0 kJ/mol*	gas
Carbon Monoxide	6		-282.99 kJ/mol*	gas
Hydrogen	6		-285.84 kJ/mol*	gas

Heat of Reaction (25C) 601.4724 kJ/mol Dry Cellulose

[‡] Value provided in problem statement
* Value obtained from Felder and Rousseau (2005)

Dry Cellulose (1450 C)

Heat Capacities

Species	State	Temp Unit	a*E3	b*E5	c*E8	d*E12	Tin, C or K	Tf, C or K	Delta H
Dry cellulose	s	K	-11.704	67.207	0	0	298.15	1723.15	951.2211 kJ/mol
Water	g	C	33.46	0.688	0.7604	-3.593	100	1450	56.12328 kJ/mol
	l	C	75.4	0	0	0	25	100	5.655 kJ/mol
Carbon Monoxide	g	C	28.95	0.411	0.3548	-2.22	25	1450	46.72521 kJ/mol
Hydrogen	g	C	28.84	0.00765	0.3288	-0.8698	25	1450	43.55743 kJ/mol

Heat capacity equations of the following form, all values obtained from Felder and Rosseau (2005)

$$C_{p,i} = a \times 10^3 + b \times 10^6 T + c \times 10^8 T^2 + d \times 10^{12} T^3$$

Heat of Vaporization	Tm	Delt H
Water	100 C	2256.9 kJ/kg[‡]
		40.6603104 kJ/mol

[‡] Value obtained from Felder and Rousseau (2005)

$$\boxed{\begin{aligned}\Delta\widetilde{H}_r(1450°C) = \int_{1723.15}^{298.15} C_{p,cellulose}\,dT + \int_{1450}^{100} C_{p,H_2O}\,dT + \Delta\widetilde{H}_{vap}(25°C) + \int_{100}^{25} C_{p,H_2O}\,dT \\ + \Delta\widetilde{H}_r(25°C) + 6\int_{25}^{1450} C_{p,CO}\,dT + 6\int_{25}^{1450} C_{p,H_2}\,dT\end{aligned}}$$

Heat of Reaction (1450C)	89.50862 kJ/mol	Dry Cellulose

Heat of Reaction of Lignin and Steam

Lignin (25 C)

$$\boxed{C_{10}H_{12}O_{3(s)} + 7H_2O_{(g)} \longrightarrow 10CO_{(g)} + 13H_{2(g)}}$$

Species	Stoichiometric Coefficient	ΔH combustion		State
Dry cellulose	1	-21178 J/g[Ŧ]	-3816.49 kJ/mol	solid
Water	7		0 kJ/mol*	gas
Carbon Monoxide	10		-282.99 kJ/mol*	gas
Hydrogen	13		-285.84 kJ/mol*	gas

Heat of Reaction (25C)	2729.333 kJ/mol	Lignin

[Ŧ] Value provided in problem statement

* Value obtained from Felder and Rousseau (2005)

Lignin (1450 C)

Heat Capacities

Species	State	Temp Unit	a*E3	b*E5	c*E8	d*E12	Tin, C or K	Tf, C or K	Delta H
Lignin	s	K	31.43	39.44	0	0	298.15	1723.15	612.7933 kJ/mol
Water	g	C	33.46	0.688	0.7604	-3.593	100	1450	56.12328 kJ/mol
	l	C	75.4	0	0	0	25	100	5.655 kJ/mol
Carbon Monoxide	g	C	28.95	0.411	0.3548	-2.22	25	1450	46.72521 kJ/mol
Hydrogen	g	C	28.84	0.00765	0.3288	-0.8698	25	1450	43.55743 kJ/mol

Heat capacity equations of the following form, all values obtained from Felder and Rosseau (2005)

$$\boxed{C_{p,i} = a \times 10^3 + b \times 10^6 T + c \times 10^8 T^2 + d \times 10^{12} T^3}$$

Heat of Vaporization	Tm	Delt H
Water	100 C	2256.9 kJ/kg[‡]
		40.6603104 kJ/mol

[‡] Value obtained from Felder and Rousseau (2005)

$$\Delta\widehat{H_r}(1450°C) = \int_{1723.15}^{298.15} C_{p,lignin}\,dT + 7\int_{1450}^{100} C_{p,H_2O}\,dT + 7\Delta\widehat{H}_{vap}(25°C) + 7\int_{100}^{25} C_{p,H_2O}\,dT + \Delta\widehat{H_r}(25°C) + 10\int_{25}^{1450} C_{p,CO}\,dT + 13\int_{25}^{1450} C_{p,H_2}\,dT$$

Heat of Reaction (1450C)	2432.968 kJ/mol	Lignin

Heat of Reaction of Methane and Steam

Methane (25 C)

$$CH_{4(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3H_{2(g)}$$

Species	Stoichiometric Coefficient	ΔH combustion	State
Methane	1	-890.36 kJ/mol*	solid
Water	1	0 kJ/mol*	gas
Carbon Monoxide	1	-282.99 kJ/mol*	gas
Hydrogen	3	-285.84 kJ/mol*	gas

Heat of Reaction (25C)	250.15 kJ/mol	Lignin

* Value obtained from Felder and Rousseau (2005)

Methane (1450 C)

Heat Capacities

Species	State	Temp Unit	a*E3	b*E5	c*E8	d*E12	Tin, C or K	Tf, C or K	Delta H
Methane	g	C	34.31	5.469	0.3661	-11	25	1450	97.93145 kJ/mol
Water	g	C	33.46	0.688	0.7604	-3.593	100	1450	56.12328 kJ/mol
	l	C	75.4	0	0	0	25	100	5.655 kJ/mol
Carbon Monoxide	g	C	28.95	0.411	0.3548	-2.22	25	1450	46.72521 kJ/mol
Hydrogen	g	C	28.84	0.00765	0.3288	-0.8698	25	1450	43.55743 kJ/mol

Heat capacity equations of the following form, all values obtained from Felder and Rosseau (2005)

$$C_{p,i} = a \times 10^3 + b \times 10^6 T + c \times 10^8 T^2 + d \times 10^{12} T^3$$

Heat of Vaporization	Tm	Delt H
Water	100 C	2256.9 kJ/kg‡
		40.6603104 kJ/mol

‡ Value obtained from Felder and Rousseau (2005)

$$\Delta\widehat{H_r}(1450°C) = \int_{1450}^{100} C_{p,methane}\,dT + \int_{1450}^{100} C_{p,H_2O\,(g)}\,dT + \Delta\widehat{H}_{vap}(25°C) + \int_{100}^{25} C_{p,H_2O\,(l)}\,dT + \Delta\widehat{H_r}(25°C) + \int_{25}^{1450} C_{p,CO}\,dT + 3\int_{25}^{1450} C_{p,H_2}\,dT$$

Heat of Reaction (1450C)	227.1775 kJ/mol	Methane

Biomass Feed Rate Calculations

Feed Composition

		Calculations based on 100 g		
Component	wt%	MW (g/mol)	mol	mol frac
Cellulose	68.25	162.1436	0.42092318	0.562333
Lignin	21.75	180.2045	0.12069621	0.161244
Ash	8.78	60.086	0.14612389	0.195215
N	0.61	14.0067	0.04355059	0.058182
S	0.01	32.065	0.00031187	0.000417
Cl	0.6	35.453	0.01692381	0.022609
total			0.74852955	

Initial Feed Rate (mol/s) All Calculations assume solar and down-stream processes run 24 hrs/day

Biomass	18.03130553	64912.6999	mol/hr
Methane	81.18976561	292283.156	mol/hr
Water	166.6666667	600000	mol/hr
Ratio Methane/Biomass	4.502711436		

Gasification Reaction Assuming 100% conversion of cellulose, lignin, methane, N, S, Cl

Substance	n,in mols/s	n,out mols/s	
Cellulose	10.13960574	-	
Lignin	2.907447313	-	
Ash	3.519973925	3.51997393	
N	1.049088755	-	
S	0.007512543	-	
Cl	0.407677256	-	
H2	0.211351171	342.203746	
CH4	81.18976561	-	
H2O	166.6666667	54.9851641	*Assume no water-gas-shift rxn
CO	-	171.101873	
H2S	-	0.00751254	
N2	-	0.52454438	
HCl	-	0.20383863	

Water-Gas-Shift Equilibrium Constant

T	1073.15	T is the temperature in Kelvin
K_eq	0.937779605	

$$K_{eq} = exp\left[-4.33 + \frac{4577.8}{T}\right]$$

We can solve for x using the following eq by inserting the feed concentrations and setting Keq equal to 0.94

x 15.89066168 mols/s *The feed rate of CO2

K_eq 0.937779514 Use solver to set equal to value calculated above

$$K_{eq} = \frac{[x][H_{2,0}+x]}{[CO_0 - x][H_2O_0 - x]}$$

Water-Gas-Shift Reaction — Equilibrium Constant Calculated First

Substance	n,in mols/s	n,out mols/s
Ash	3.519973925	3.51997393
H2	342.2037463	358.094408
H2O	54.98516413	39.0945024
CO	171.1018732	155.211211
H2S	0.007512543	0.00751254
N2	0.524544378	0.52454438
HCl	0.203838628	0.20383863
CO2	-	15.8906617

Ash Removal — Assume 100% removal of ash

Substance	n,in mols/s	n,out mols/s
Ash	3.519973925	-
H2	358.094408	358.094408
H2O	39.09450245	39.0945024
CO	155.2112115	155.211211
H2S	0.007512543	0.00751254
N2	0.524544378	0.52454438
HCl	0.203838628	0.20383863
CO2	15.89066168	15.8906617

ZnO Reactor **Assume 100% removal of hydrogen sulfide and hydrogen chloride**

Substance	n,in mols/s	n,out mols/s	
H2	358.094408	358.094408	
H2O	39.09450245	39.2039343	Water added that was generated
CO	155.2112115	155.211211	
H2S	0.007512543	-	
N2	0.524544378	0.52454438	
HCl	0.203838628	-	
CO2	15.89066168	15.8906617	
ZnO	0.109431857	-	
ZnS	-	0.00751254	Solid Product Removed
ZnCl2	-	0.10191931	Solid Product Removed

Methanol Reactor **Assume all of the carbon sources form methanol for simplification purposes**

Substance	n,in mols/s	n,out mols/s
H2	358.094408	1.4211E-13
H2O	39.20393431	55.094596
CO	155.2112115	-
N2	0.524544378	0.52454438
CO2	15.89066168	-
CH3OH	-	171.101873

Methanol Produced 5395868672 mols/yr *CH3OH from cell above

Annual feed rate calculations for a target 56 M gallons of 99.97% methanol

Ratio H2/CO	2		
Methanol Properties			
Density	0.7918	g/cm3	
MW	32.04	g/mol	
Methanol	56000000	gallons/yr	
	211983059.7	L/yr	
	2.11983E+11	cm3/yr	
	1.67848E+11	g/yr	
	5238707449	mol/yr	
Annual Methanol Production	5395868672	mol/yr	Multiplied by 1.03 to get pure methanol

Feed Rate	24 hr process	8 hr process (multiply 24 hr process by three)		
Component	mol/hr	mol/hr	mol/s	kg/hr
Cellulose	36502.58	109507.74	30.4188172	17755.98
Lignin	10466.81	31400.43	8.72234194	5658.50
Ash	12671.91	38015.72	10.5599218	2284.21
N	3776.72	11330.16	3.14726627	158.70
S	27.05	81.14	0.02253763	2.60
Cl	1467.64	4402.91	1.22303177	156.10
Biomass	64912.70	194738.10	54.0939166	26016.09
Methane	292283.16	876849.47	243.569297	14029.59
Water	600000.00	1800000.00	500	32428.80

All calculations were performed using the Solver function on EXCEL™ specifying K_{eq}=0.9378, Annual Methanol Production = 5395868672 mol/yr, and Ratio H_2/CO = 2, while varying Biomass and Methane feed rate and x (the flow rate of CO_2 out of the gasification chamber).

Theoretical Solar Reactor Energy Requirement Calculations

References

Temperature	25 C
Pressure	1 atm

Initial Flowrates

Component	mols/hr	kg/hr	mols/s	kg/s
Cellulose	109507.74	17755.98	30.41882	4.932217
Lignin	31400.43	5658.50	8.722342	1.571805
Ash	38015.72	2284.21	10.55992	0.634503
CH4	876849.47	14029.59	243.5693	3.897109
H2O	1800000.00	32428.80	500	9.008

*Flowrates calculated on spread sheet "Biomass Feed Rate"

Heat Capacities

Heat capacities of the form

$$\boxed{C_{p,i} = a \times 10^3 + b \times 10^6 T + c \times 10^8 T^2 + d \times 10^{12} T^3}$$

Component	State	Temp Unit	a*E3	b*E5	c*E8	d*E12	Tin, C or K	Tf, C or K	H1	H2	Delta H
Cellulose‡	s	K	-11.704	67.207	0	0	298.15	1723.15			951.2211 kJ/mol
Lignin‡	s	K	31.43	39.44	0	0	298.15	1723.15			612.7933 kJ/mol
Ash‡	s	K	705	J/kg*K			298.15		12.63		
	s	K	42360.63	J/kmol*K			1723.15			72.99	60.3639 kJ/mol
Methane*	g	C	34.31	5.469	0.3661	-11	25	1450			97.93145 kJ/mol
Water*	l	C	75.4	0	0	0	25	100			5.655 kJ/mol
	g	C	33.46	0.688	0.7604	-3.593	100	1450			56.12328 kJ/mol

‡ Value given in problem statement

* Coefficients obtained from Felder and Rousseau (2005)

Heat of Vaporization

Component	Tm	Delt H
Water*	100 C	2256.9 kJ/kg
		40.66031 kJ/mol

* Value obtained from Felder and Rousseau (2005)

Heats of Reaction (1450 C)

Component	
Dry Cellulose	89.5086216 kJ/mol
Lignin	2432.96795 kJ/mol
Methane	227.177467 kJ/mol

Theoretical Solar Reactor Energy Calculation

The energy required to power the solar reactor is given by the following equation

$$
\begin{aligned}
E_{solar} = n_{cellulose}&\left[\int_{298.15}^{1723.15} C_{p,cellulose}\,dT + \Delta\hat{H}_{rxn,cellulose}(1450^{\circ}C)\right] \\
&+ n_{lignin}\left[\int_{298.15}^{1723.15} C_{p,lignin}\,dT + \Delta\hat{H}_{rxn,lignin}(1450^{\circ}C)\right] \\
&+ n_{ash}\int_{1723.15}^{298.15} C_{p,ash}\,dT \\
&+ n_{H_2O}\left[\int_{25}^{100} C_{p,H_2O(l)}\,dT + \Delta\hat{H}_{vap,H_2O}(25^{\circ}C) + \int_{100}^{1450} C_{p,H_2O(g)}\,dT\right] \\
&+ n_{CH_4}\left[\int_{100}^{1450} C_{p,CH_4}\,dT + \Delta\hat{H}_{rxn,CH_4}(1450^{\circ}C)\right]
\end{aligned}
$$

Substance	n,in	H,in	n,in*H,in
Cellulose	30.4188172 mols/s	1040.73 kJ/mol	31657.77
Lignin	8.72234194 mols/s	3045.761 kJ/mol	26566.17 kJ/s
Ash	10.5599218 mols/s	60.3639 kJ/mol	637.438 kJ/s
CH4	243.569297 mols/s	325.1089 kJ/mol	79186.55 kJ/s
H2O	500 mols/s	102.4386 kJ/mol	51219.3 kJ/s
Totals			189267.2 kJ/s
			0.189267 GW

Total annual plant operation	2920 hr*
Annual Net Energy Required	552.6603 GW-hr

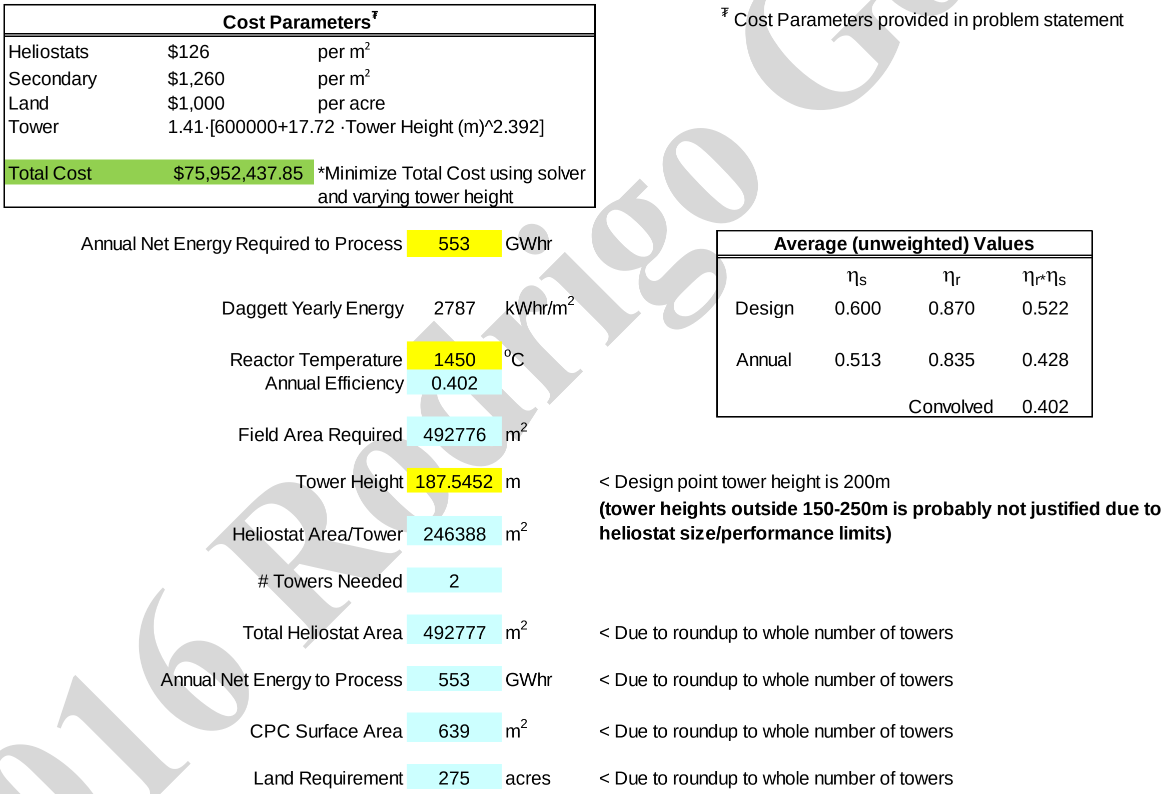
*Hours of operation on an annual basis provided in problem statement

Appendix B. Optimal Solar Field Calculations

The optimal solar field configuration was calculated using EXCEL™ spreadsheets provided by Mr. Allan Lewandowski, a professional solar field designer. The spreadsheets provide performance calculations at a given temperature for a solar field that utilizes a central receiver. The data used is direct data from TMY Data Set for the Mojave Desert Location in Daggett, California.[26]

The following output was generated given an input of 553 GW-hr required to power the gasification reaction and a reactor temperature of 1450 °C. The EXCEL™ Solver function was used to minimize Total Cost by varying Tower Height using the spreadsheet for a total sun concentration of 4000 suns.

Scaling Inputs and Costing



Cost Parameters[‡]		
Heliostats	$126	per m^2
Secondary	$1,260	per m^2
Land	$1,000	per acre
Tower	1.41·[600000+17.72 ·Tower Height (m)^2.392]	
🟩 Total Cost	$75,952,437.85	*Minimize Total Cost using solver and varying tower height

[‡] Cost Parameters provided in problem statement

Annual Net Energy Required to Process	553	GWhr	
Daggett Yearly Energy	2787	$kWhr/m^2$	
Reactor Temperature	1450	^oC	
Annual Efficiency	0.402		
Field Area Required	492776	m^2	
Tower Height	187.5452	m	< Design point tower height is 200m **(tower heights outside 150-250m is probably not justified due to heliostat size/performance limits)**
Heliostat Area/Tower	246388	m^2	
# Towers Needed	2		
Total Heliostat Area	492777	m^2	< Due to roundup to whole number of towers
Annual Net Energy to Process	553	GWhr	< Due to roundup to whole number of towers
CPC Surface Area	639	m^2	< Due to roundup to whole number of towers
Land Requirement	275	acres	< Due to roundup to whole number of towers

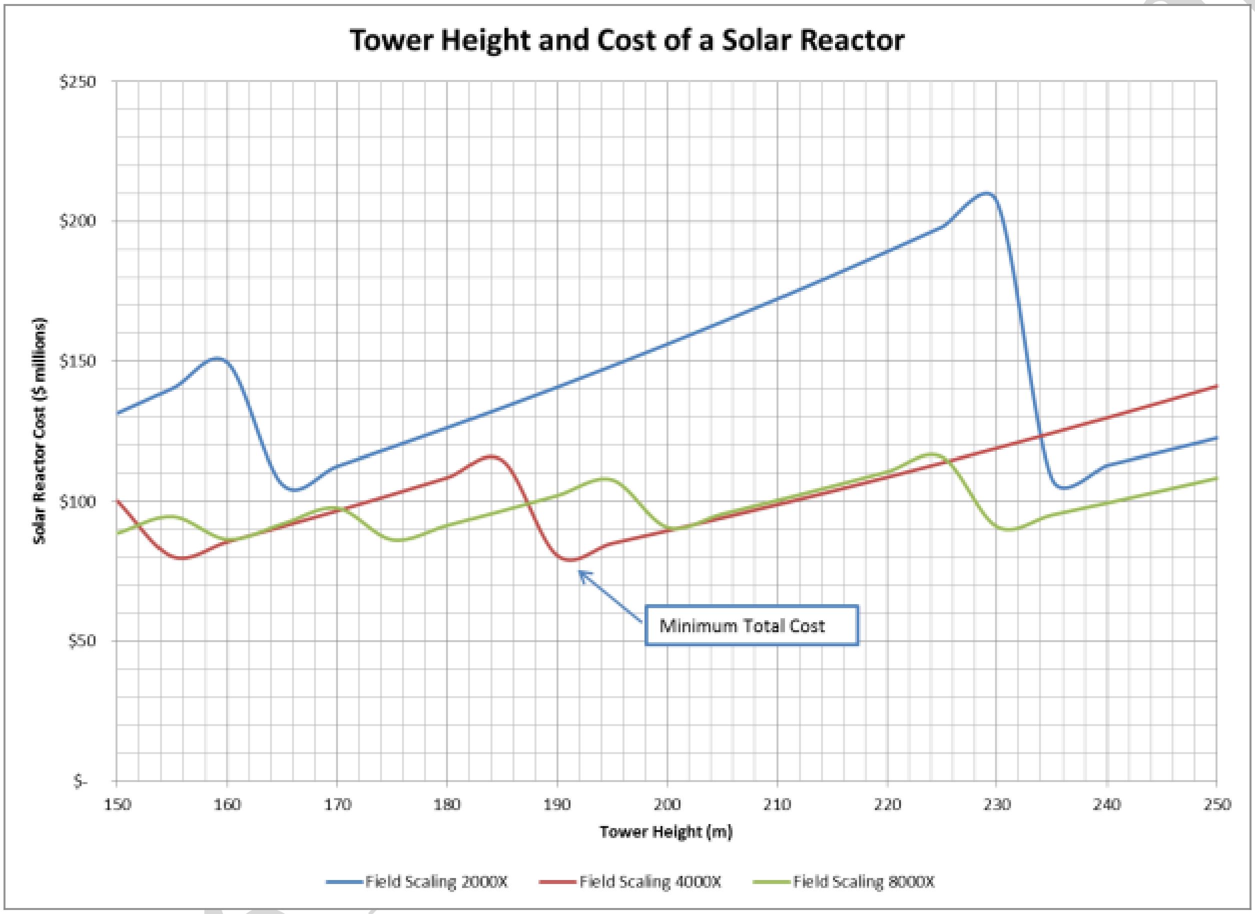
Average (unweighted) Values			
	η_s	η_r	$\eta_r * \eta_s$
Design	0.600	0.870	0.522
Annual	0.513	0.835	0.428
		Convolved	0.402

---

[26] Data collected by Mr. Allan Lewandowski

Field Concentration Selection

A Field Scaling size of 4000 suns was chosen by varying the tower height in the 2000, 4000, and 8000X spreadsheets, and calculating total cost using the cost parameters provided in the problem statement. The following figure summarizes the results and shows that Total Cost is minimized using the 4000X solar concentration field.



Design Point Performance

Design Point
Baseline Parameters @ I=1000W/m^2
D82H10

			Scaling Factors	New Parameters	
Tower Height	200	m		187.5452	m
Lookout Angle	35	deg		35	deg
CPC Acceptance	35	deg		35	deg
Heliostat Area	100	m^2	2	88	m^2
Tower Height/Heliostat Dimension	20			20	
# Heliostats/Field	934			934	
Total Heliostat Area/Field	93400	m^2	2	82129	m^2
Land Area/Field	52.2	acres	2	45.9	acres
Delivered Power to Aperture	61220	kW	2	53832	kW
Field Efficiency to Aperture	0.658			0.658	
CPC Concentration	2.97			2.97	
CPC Throughput	0.915			0.915	
Delivered Power to Reactor	56019	kW	2	49259	kW
Net Concentration	3868			3868	
CPC Surface Area	120.2	m^2	1.9	106.4	m^2
# Fields per Reactor	3			3	
Total CPC Area	360.7	m^2		319.3	m^2
Total Number of Heliostats	2802			2802	
Total Heliostat Area	280200	m^2		246388	m^2
Total Land Area	156.6	acres		138	acres
Total Power to Aperture	183659	kW		161497	kW
Total Power to Reactor	168058	kW		147778	kW
Design Point Efficiency to Receiver	0.603			0.603	
Reactor Temperature	1450	C		1450	C
Annual Efficiency	0.402			0.402	
Solar Available	2787	kWhr/m^2		2787	kWhr/m^2

# Towers	2	

Total CPC Area	639	m^2
Total Number of Heliostats	5604	
Total Heliostat Area	492777	m^2
Total Land Area	275	acres

At Design Point

Total Power to Aperture	323	MW
Total Power to Reactor	296	MW

Design Point Calculations

Soltrace analysis to generate design point

L30D82H10

T	200		
s	10	ρ	0.92
T/s	20.0		
θ_c	30	C	4.00
Focal Lengths	3		

γ	CPC Entrance Diameter, m for ~95% power
30	5.35
35	6.05
40	7.25
45	9.20

σ_{slope}	1.3
σ_{spec}	0.5

γ	C/C_{max}	#	Area, m^2	Proj Area, m^2	Total Power, kW	η_{tp}	s/b	95% Power, kW	95% Intercept Entrance Radius, m	95% Intercept Exit Radius, m	95% Intercept Height, m	~CPC Surface Area, m^2	C	Ideal Exit Flux, kW/m^2	Fraction of Ideal	CPC Entrance Power, kW	CPC Exit Power, kW	CPC Exit Flux, kW/m^2	CPC Throughput	Solar Efficiency	Fraction of Ideal	Ellipse Area, m^2	Heliostat Area Fraction	Enclosing Rectangle Area, acres
30.0	0.333	422	42200	40011	35762	0.847	0.028	33974	2.675	1.354	5.628	69.25	3.90	5899	0.128	33778	30711	5332	0.904	0.728	0.115	83119	0.51	23.1
35.0	0.266	551	55100	51982	44303	0.804	0.074	42088	3.025	1.531	6.365	88.56	3.90	5714	0.124	42047	38666	5250	0.919	0.702	0.114	111817	0.49	31.6
40.0	0.199	764	76400	71495	57233	0.749	0.130	54371	3.625	1.835	7.627	127.17	3.90	5141	0.111	54990	50609	4785	0.931	0.662	0.103	165202	0.46	44.3
45.0	0.134	1199	119900	110805	79823	0.666	0.217	75832	4.600	2.328	9.679	204.79	3.90	4452	0.096	75503	69494	4080	0.916	0.580	0.088	280993	0.43	70.8

T	200		
s	10	ρ	0.92
T/s	20.0		
θ_c	35	C	3.04
Focal Lengths	3		

γ	CPC Entrance Diameter, m for ~95% power
35	7.40
40	9.33
45	12.90

γ	C/C_{max}	#	Area, m^2	Proj Area, m^2	Total Power, kW	η_{tp}	s/b	95% Power, kW	95% Intercept Entrance Radius, m	95% Intercept Exit Radius, m	95% Intercept Height, m	~CPC Surface Area, m^2	C	Ideal Exit Flux, kW/m^2	Fraction of Ideal	CPC Entrance Power, kW	CPC Exit Power, kW	CPC Exit Flux, kW/m^2	CPC Throughput	Solar Efficiency	Fraction of Ideal	Ellipse Area, m^2	Heliostat Area Fraction	Enclosing Rectangle Area, acres
35.0	0.174	934	93400	87242	70852	0.759	0.117	67309	3.700	2.147	6.728	120.24	2.97	4650	0.101	67333	62082	4289	0.922	0.665	0.093	205388	0.45	52.24
40.0	0.114	1427	142700	131793	96655	0.677	0.203	91822	4.665	2.706	8.483	191.14	2.97	3990	0.086	91811	84592	3676	0.921	0.593	0.079	345660	0.41	81.45
45.0	0.060	2638	263800	239508	142613	0.541	0.353	133169	6.450	3.742	11.729	365.40	2.97	3080	0.067	134939	124130	2822	0.932	0.471	0.061	747036	0.35	153.55

T	200		
s	10	ρ	0.92
T/s	20.0		
θ_c	40	C	2.42
Focal Lengths	3		

γ	CPC Entrance Diameter, m for ~95% power
40	13.20

γ	C/C_{max}	#	Area, m^2	Proj Area, m^2	Total Power, kW	η_{tp}	s/b	95% Power, kW	95% Intercept Entrance Radius, m	95% Intercept Exit Radius, m	95% Intercept Height, m	~CPC Surface Area, m^2	C	Ideal Exit Flux, kW/m^2	Fraction of Ideal	CPC Entrance Power, kW	CPC Exit Power, kW	CPC Exit Flux, kW/m^2	CPC Throughput	Solar Efficiency	Fraction of Ideal	Ellipse Area, m^2	Heliostat Area Fraction	Enclosing Rectangle Area, acres
40.0	0.114	3024	302400	228669	162683	0.538	0.227	154549	6.600	4.286	10.444	348.32	2.37	2678	0.058	154617	142885	2475	0.925	0.473	0.054	899041	0.34	170.1

Current Analysis

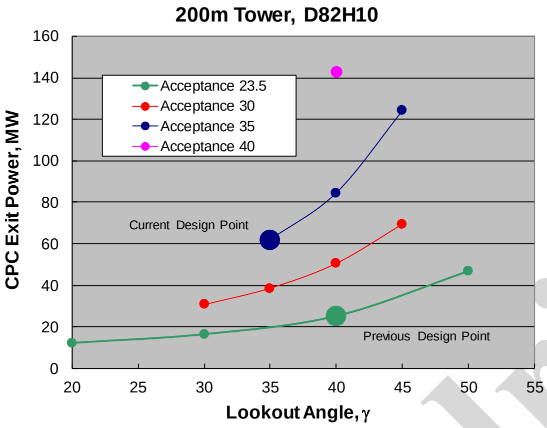
θ_c	30		
γ	30.0	30.7	0.728
	35.0	38.66584	0.701739
	40.0	50.60943	0.662427
	45.0	69.49445	0.579603

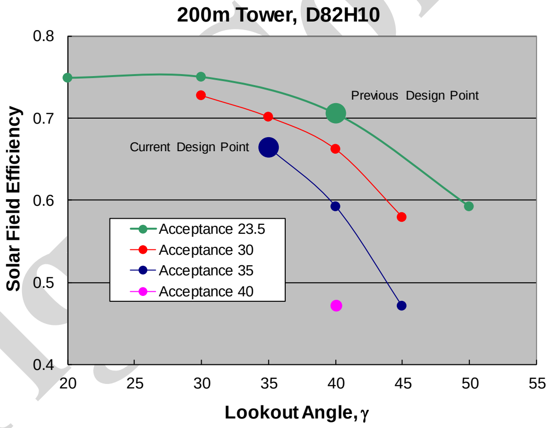
7000x analysis

θ_c	23.5		
γ	20	12.29	0.749
	30	16.509	0.750
	40	25.267	0.706
	50	46.868	0.593

θ_c	35		
γ	35.0	62.1	0.665
	40.0	84.6	0.593
	45.0	124.1	0.471

θ_c	40		
γ	40	142.9	0.473





Annual Performance Summary

Reactor Temperature **1450** ^{o}C

	Month											
Hour	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
6					0.00	1.04	0.00					
7			0.15	2.87	4.66	6.10	4.57	2.81	1.62			
8	0.29	2.26	5.59	7.83	8.78	9.87	8.64	7.65	7.26	4.94	2.73	0.49
9	4.81	5.74	9.74	11.78	11.39	12.37	11.31	10.86	11.14	8.89	6.92	4.63
10	7.88	7.85	11.30	13.41	12.61	13.38	12.85	12.71	13.23	11.06	9.09	7.14
11	9.44	8.82	12.60	14.13	13.70	14.12	13.55	12.91	13.71	12.37	10.68	8.94
12	10.40	9.34	12.34	14.79	14.24	14.28	13.78	13.61	13.82	12.07	11.09	9.32
13	9.98	8.88	12.39	13.65	14.04	13.60	14.01	12.77	13.18	11.39	9.93	8.80
14	8.84	8.62	11.44	13.17	13.23	13.47	13.23	12.26	11.94	10.95	8.03	7.30
15	6.67	7.19	9.91	12.07	11.77	11.73	12.54	10.81	10.28	8.82	5.64	4.86
16	2.66	4.47	6.55	8.44	9.45	9.83	10.00	7.57	6.01	5.14	2.33	0.95
17			1.91	4.32	5.85	6.46	6.05	3.47	1.87			
18					1.02	2.02	1.48					
# Days	31	28	31	30	31	30	31	30	31	31	30	31
Monthly Sum, kWhr/m^2	61.0	63.2	93.9	116.4	120.7	128.3	122.0	107.4	104.1	85.6	66.4	52.4
$\eta_{monthly}$	0.344	0.372	0.411	0.427	0.434	0.436	0.429	0.417	0.412	0.387	0.362	0.315
η_{annual}	**0.402**											

Clear Day Direct Irradiance

ASHRAE Handbook of Fundamentals, 1972; Clear Day Direct Irradiance, W/m^2; α>10^o; L=30

Modeled Day	22	53	82	112	142	173	203	234	264	295	326	356
# Days	31	28	31	30	31	30	31	30	31	31	30	31
	Month											
Hour	1	2	3	4	5	6	7	8	9	10	11	12
5												
6					375	413	356					
7			583	649	665	662	640	599	514			
8	640	779	820	804	788	772	760	756	756	722	618	555
9	848	908	914	876	848	832	823	829	857	860	829	810
10	930	965	958	914	883	864	854	870	905	924	911	908
11	965	993	980	930	898	879	873	889	927	952	949	949
12	977	999	987	936	901	883	879	895	933	958	958	958
13	965	993	980	930	898	879	873	889	927	952	949	949
14	930	965	958	914	883	864	854	870	905	924	911	908
15	848	908	914	876	848	832	823	829	857	860	829	810
16	640	779	820	804	788	772	760	756	756	722	618	555
17			583	649	665	662	640	599	514			
18					375	413	356					
19												
Monthly Sum, kWhr/m^2	240	232	294	278	304	292	294	263	274	244	227	229
Yearly Sum, kWhr/m^2	3174											
Daily Average, kWhr/m^2	8.69											

Direct Data from TMY Data Set for Mojave Desert Location

Daggett TMY2 Average Hourly Values, W/m^2 **N34 52** **W116 47** **Data from Daggett.xls**

Modeled Day	**22**	**53**	**82**	**112**	**142**	**173**	**203**	**234**	**262**	**295**	**326**	**356**
# Days	**31**	**28**	**31**	**30**	**31**	**30**	**31**	**30**	**31**	**31**	**30**	**31**
	Month											
Hour	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
5	0	0	0	0	15	41	13	0	0	0	0	0
6	0	0	12	155	297	409	297	179	79	9	0	0
7	3	71	273	511	550	642	543	505	476	325	119	24
8	264	387	557	681	676	750	667	669	673	581	496	348
9	518	545	692	798	736	812	732	746	771	704	673	551
10	655	629	737	847	770	837	782	809	840	763	739	650
11	692	665	780	871	806	854	798	807	838	807	779	690
12	723	684	768	890	829	859	807	829	845	777	775	683
13	724	668	769	846	823	826	821	799	810	753	732	681
14	717	677	744	834	802	842	802	785	771	757	668	661
15	653	646	701	814	756	777	797	743	722	699	567	568
16	523	581	624	722	717	748	749	663	587	596	461	409
17	240	426	511	653	643	670	659	570	505	343	107	109
18	3	84	205	429	457	528	519	403	230	19	0	0
19	0	0	1	37	108	217	197	74	2	0	0	0
Monthly Sum, kWhr/m^2	177	170	229	273	279	294	285	257	253	221	183	167
Yearly Sum, kWhr/m^2	2787											
Daily Average, kWhr/m^2	7.64											

Daggett TMY2 Maximum Hourly Values, W/m^2

# Days	**31**	**28**	**31**	**30**	**31**	**30**	**31**	**30**	**31**	**31**	**30**	**31**
	Month											
Hour	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
5	0	0	0	0	63	87	50	0	0	0	0	0
6	0	0	72	376	537	550	499	330	173	51	0	0
7	16	250	598	744	782	778	749	716	681	578	329	79
8	526	750	832	876	886	879	857	848	857	821	768	600
9	812	906	936	948	925	932	916	917	930	916	906	829
10	923	965	995	989	968	964	948	959	975	966	969	932
11	977	1008	1021	1007	992	980	969	980	1000	990	997	977
12	992	1017	1031	1021	994	987	979	995	1008	1001	1004	987
13	987	1029	1031	1020	986	990	981	1000	1004	998	996	986
14	970	1005	1018	1006	979	976	971	985	984	970	972	960
15	914	979	987	978	952	955	951	959	954	933	905	893
16	815	913	928	930	908	917	914	922	896	845	763	737
17	560	752	805	835	830	847	849	839	774	636	314	256
18	46	257	475	618	680	718	720	649	447	102	0	0
19	0	0	8	114	257	398	373	206	27	0	0	0
Monthly Sum, kWhr/m^2	265	275	333	344	364	359	364	339	332	304	268	255
Yearly Sum, kWhr/m^2	3801											
Daily Average, kWhr/m^2	10.41											

Appendix C. Equipment Sizing and Costing

Cutters Sizing and Costing

Equipment	**Cutters**
Type	Rotary cutter
Specifics	Motor, drive, guard included

Cost Equation y = -12.4592725409836*x^2+3040.98360655738*x+9912.3975409836100

y Purchased Cost, $

Size Factor (x)

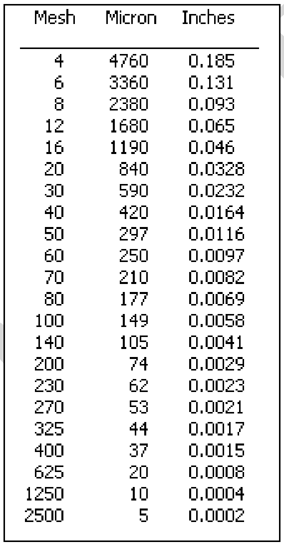
Units	Minimum	Maximum	CE
Capacity, kg/s	1	100	500

Total mass flow	317.397894	kg/hr
Total mass flow	5.2899649	kg/s
max flow	100	
Cost	$ 25,650.44	
2010 cost	$ 28,523.29	

Grinder Sizing and Costing

Grinder Specifications

http://www.espi-metals.com/tech/mesh.htm



Mesh	Micron	Inches
4	4760	0.185
6	3360	0.131
8	2380	0.093
12	1680	0.065
16	1190	0.046
20	840	0.0328
30	590	0.0232
40	420	0.0164
50	297	0.0116
60	250	0.0097
70	210	0.0082
80	177	0.0069
100	149	0.0058
140	105	0.0041
200	74	0.0029
230	62	0.0023
270	53	0.0021
325	44	0.0017
400	37	0.0015
625	20	0.0008
1250	10	0.0004
2500	5	0.0002

The primary design specification of a ball grinder mill is the outlet particle size. Here, we are shooting for between 150 and 300 um.

This gives us a mesh grade of 100~40.

Grinder Costing

Equipment	Type	Specifics
Grinders	Ball mill dry grinding. Closed circuit with air classifier. **	0.013 m (1/2-in.) to 100 mesh

Cost Equation

y = 1.28073770491803*(10^(0.1991*log10(x)^3 + 0.0693*log10(x)^2 + 0.5601*log10(x) + 5.1962))

	Size Factor (x)			
y	Units	Minimum	Maximum	CE
Purchased Cost, $ (allowance for foundations and erection included)	Capacity, kg/s	0.252	3.78	500

Total capacity	317.397894	kg/h
Total capacity	5.2899649	kg/s
max capacity	3.78	

cost	$	488,168.42
Economy of scale cost	$	597,236.40
2010 cost	$	664,126.88

* from Seider, Warren D., J.D. Seader, and Daniel R. Lewin. Product & Process Design Principles. 2nd ed. New York: Wiley. 1999

** Includes installation, classifier, motors, drives. Does not include freight, auxiliary equipment, or handling equipment

*** from Harrison, Roger G., et al. Bioseparations Science and Engineering. New York: Oxford. 2003

if not cited above, from Peters and Timmerhaus, 2001

Solar Reactor

Sizing the Solar Reactor

The size of the reactor depends upon the volumetric flow rate of the feed that is fed into the reactor and the exposed surface area of the silicon carbide tubes

In order to calculate the volumetric flow rate, we can use the ideal gas law at the reaction temperature of 1450 C

$$\boxed{\dot{V} = \frac{RT\dot{n}}{P}}$$

Total Molar Feed Rate

Component		
Biomass	54.09391659	mols/s
Methane	243.5692968	mols/s
Water	500	mols/s
Total	797.6632134	mols/s

Ideal Gas Law Parameters and Constant

Parameter	Value	Unit	
R	8.31E-05	m^3 bar K^{-1} mol^{-1}	
T	1450	C	
	1723.15	K	
P	35	bar	
$\dot{V}$	3.265196174	m^3/s	*Calculated from feed rate
	7.430332286	m^3/s	*Exit volumetric flowrate from ASPEN Plus™

Since the solar reactor effluent volumetric flow rate is greater this value will be used

Volume of Silicon Carbide Tubes in Solar Reactor

Parameter	Value	Unit	
$\dot{V}$	7.430332286	m^3/s	Volumetric flow rate
τ*	1	s	Residence time
Vol	7.430332286	m^3	

$$\boxed{Vol = \dot{V} \times \tau}$$

* Residence time for the solar reactor given specifications from problem statement from "Rapid High Temperature Solar-Thermal Biomass Gasification in a Prototype Cavity Reactor" Lichty et al. 2010

Silicon Carbide Tube Specifications

Parameter	Value	Unit		
Di	0.1143	m	Inner diameter	
	4.5	in		
Do	0.1524	m	Outer diameter	
	6	in		
L	5.035331892	m	Length of each SiC tube	
	5.2	m	Length of Manufactured tubes	*Approx. 3% larger to allow installation space
N	72		Number of tubes per tower	
N_T	2		Number of towers	
N_{tot}	144		Total number of silicon carbide tubes	
Volume	7.44	m^3		
SA	347.1566054	m^2	Surface Area	

Power Delivered to Carbide Tubes

Total Power At Design Point

Parameter	Value	Unit
Total Power to Aperture$^{¥}$	322.9945	MW
Total Power to Reactor$^{¥}$	295.5562	MW
Total Power delivered to SiC tubes*	189.2672	MW

¥ Values calculated using the EXCEL™ spreadsheet for 4000 sun concentration for the specified values given in the problem statement

* From Annual Net Energy need to power the reaction. Consult Appendix A for detailed calculations

Target Heat Flux to Silicon Carbide Tubes

Parameter	Value	Unit	
Flux	545.1926279	KW/m^2	*Use EXCEL™ solver function to set flux equal to target 500 KW/m^2 as provided in the problem statement by varying the outer diameter and length

Solar Reactor Housing Specifications

Hexagonal Aperture Specifications

Parameter	Value	Unit	
W	4	m	Height of aperature (smallest width of hexagon)
Area	13.85640646	m^2	Area of aperature
L	2.309401077	m	Length of Sides

$$Area_{hex} = \frac{\sqrt{3}}{2} W^2$$

$$L = \sqrt{\frac{2Area_{hex}}{3\sqrt{3}}}$$

Aperature Shutter Specifications

Parameter	Value	Unit	
W	2.5	m	Shutter width for central closure
H	4.5	m	Height of Aperture
Area	11.25	m^2	Total area of each shutter (6 shutters)

Costing the Carbide Tubes

In addition to costing the solar field components the reactor itself needs to be costed

Silicon Carbide Tube Costing

Parameter	Value	Unit
Length	748.8	m
	2456.6929	ft
Cost per unit length	$ 1,000.00	per ft*

Total Cost	$	2,456,692.92

*Cost of the Carbide Tubes provided in the problem statement

Costing the Solar Reactor

TC	$ 15,352,439.15

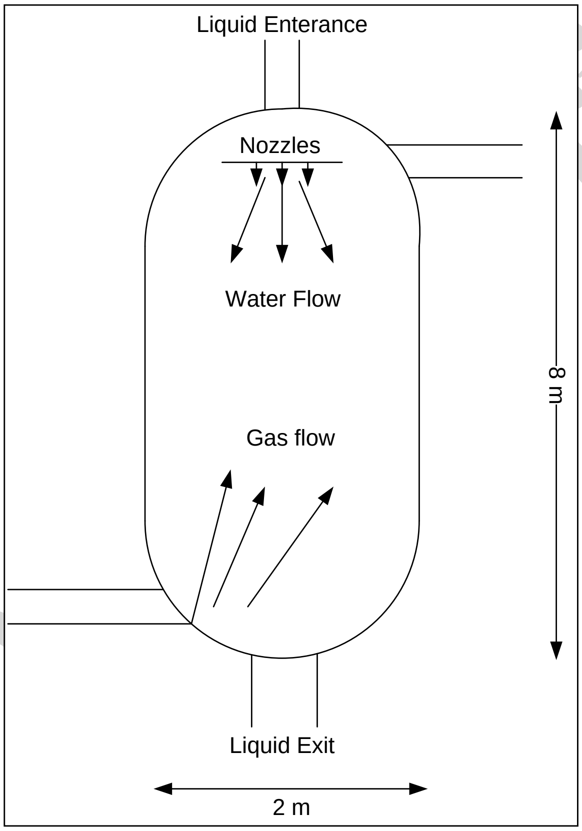
Spray Quench Tank Sizing and Costing

pl	995	kg/m^3	density of liquid droplet
lamda	32081624	j/kg	liquid heat of vaporization found using Hysys
Do	0.0005	m	droplet diameter
kg	0.24	j/msk	thermal conductivity of gas. Found in HYSYS
inlet T gas	1073.15	K	obtained via Aspen plus
inlet T liquid	305.3722	K	obtained via Aspen plus
outlet T gas	483.8889	K	obtained via Aspen plus
outlet T liquid	490.3675	K	obtained via Aspen plus
DTg	589.2611		gas temperature change
DTl	184.9953		liquid temperature change
T	348.9445	K	log mean temperature between drop and gas
Theta	11.91137	s	Evaporation time of droplets and residency time of gas in tank

$$\theta = \rho_l \lambda D^2 / 8 k_g \Delta T$$

Total gas flow rate	2.099594		obtained via Aspen plus
Total volume	25.00906	m^3	Total volume of spray quench tank
Cross section	3.141593	m^2	
Tank diameter	2	m	
tank length	7.96	m	

Water flow rate	41.11	kg/s
Gas flow rate	19.12	kg/s



Equipment	Type	Specifics		Construction Material
Storage Tanks	Horizontal storage vessels	Diameter, 2 m	5000 kPa	Nickel alloy

		Size Factor (x)			
Cost Equation	**y**	**Units**	**Minimum**	**Maximum**	**CE**
y =1.62860655737705*x^3-125.31475409836*x^2+42595.4918032786*x+106459.91803278700	Purchased Cost, $	Length of horizontal vessels, m	4.20	41.00	500

Length	7.957747155
Cost	$438,309.13
2010 cost	$487,399.75

* from Seider, Warren D., J.D. Seader, and Daniel R. Lewin. Product & Process Design Principles. 2nd ed. New York: Wiley. 1999
** Includes installation, classifier, motors, drives. Does not include freight, auxiliary equipment, or handling equipment
*** from Harrison, Roger G., et al. Bioseparations Science and Engineering. New York: Oxford. 2003
if not cited above, from Peters and Timmerhaus, 2001

Cyclone Sizing and Costing

Particle size

Assume that all particles are between 150 um and 300 um.

Cyclone Sizing and geometry

Design is based off of a stairmand method.

Assume high efficency cyclone rather than high flow rate.

Separation Efficency

	19.45	kg/s	Gas flow rate (used in pricing via economics spreadsheet)
M	0.63	kg/s	solids mass flow rate
Mc	0.63	kg/s	mass discharged from solids exit
Mf	0.00	kg/s	solids mass flow rate leaving with gass

Et	1

$Et = \frac{Mt}{M}$ (1)

Eu	320	unitless	Euler's number, given by stairmand's design rule.
St	1.40E-04	unitless	stokes number, given by stairmand's design rule.
mew	2.92E-05	Pa*s	gas viscosity, found with aspen hysys
ρf	9.24783208	kg/m^3	gas density, found with aspen plus
ρp	2200.9524	kg/m^3	solids density, found with aspen plus
q	2.10E+00	m^3/s	gas flow rate, found with aspen plus
delta P	4.75E+04	Pa	pressure drop

v	5.67	m/s	charaistic velocity
Di	0.69	m	Diameter of the cyclone

$Eu = \Delta P/(\rho f * u^2/2)$ (2)

$u = 4q/(\pi * D^2)$ (3)

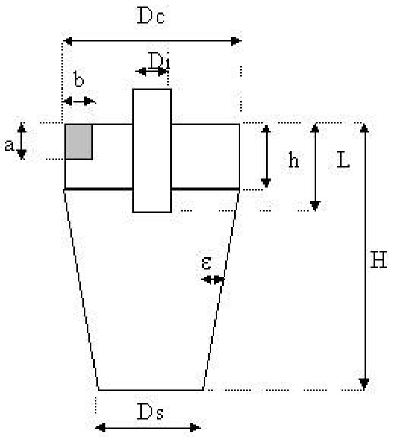
Scale up considerations

x50	2.01E-06	m	Particle size for 50% efficency
	2.01	μ m	
x	150	μ m	smallest biomass particle size
G(x)	99.98%		

$St = x_{50}^2 * \rho p * u / 18 * \mu * D$ (4)

$G(x) = (x/x_{50})^2/(1+(x/x_{50})^2)$ (5)

Geometries	Dimension Relative to D	Dimension
H	4	2.75
h	1.5	1.03
Ds	0.375	0.26
L	0.5	0.34
b	0.2	0.14
a	0.5	0.34
Dj	0.5	0.34



Equipment	**Dust Collectors**
Type	Cyclones*
Specifics	Carbon steel
Cost Equation	y = 1.26903553299492*(exp(8.9845 - 0.7892*ln(x) + 0.08487*ln(x)^2))
y	Purchased Cost, $

Units	Minimum	Maximum	CE
Gas flow rate, actual ft^3/min	200	100000	500

See message below. The cost equation for the cyclone should have a period instead of a comma in the first factor inside of the exponential. For the text, the first factor is 9.2227 instead of 9,2227. Likewise, in the Excle cost file, the factor is 8.984 instead of 8,9845.

Gas flow rate	266927.303 ft^3/hr
	4448.78838 ft^3/min

Cost	$ 5,335.57
Stainless steel cost	$ 10,671.14
2010 cost	$ 11,866.31

Zinc Oxide Fixed Bed Reactor

ZnO Kinetic Sizing Parameters

1 ZnO + H2S -> ZnS + H2O
2 ZnO +2HCl -> ZnCl2 + H2O

Kinetic Parameters

Equation	Parameter	Value	Units	Description
1	k_s	8.15E-03	mol/cm2/min	Apparent reaction rate constant (surface)
1	rho	23.14	mol/L	Molecular concentration of ZnO
1	R0	4	mm	ZnO particle size
1	k_{10}	1.47E-02	1/s	
1	Ea	11842	J/mol	Energy of Activation
2	ln k	-2.5	ln (1/s)	
2	1/T	0.0013	1/K	
2	Ea	4.88E+04	J/mol	Emergy of Activation
2	k_{20}	3.98E-05	1/s	
	R	8.314	J/mol/K	
	T	498.05	K	Average Temperature
	MW ZnO	8.14E+01	g/mol	
1	k1	2.56E-01	1/s	Reaction rate constant
2	k2	5.23E+00	1/s	Reaction rate constant
1	k'1	1.36E-04	1/s	
2	k'2	2.78E-03	1/s	

Flow through a packed bed

Parameter	Value	Units	Description
P0	35	bar	Initial pressure
	3500	kPa	
v0	2.1105762	m3/s	volumetric flowrate
phi	0.4	-	porosity (void fraction) = volume of void/total bed volume
1-phi	0.6	-	volume of solid/total bed volume
rho c	3140	kg/m3	Density of the Solid Particles
rho b	1884	kg/m3	Bulk Density
gc	1	-	Conversion factor (1 for SI)
Dp	0.004	m	Diameter of ZnO particle in the bed
mu	1.74E-05	kg/m/s	Viscosity of the gas passing through the bed
u	0.4299631	m/s	superficial velocity = volumetric fLow/cross-sectional area of the pipe
D	2.5	m	Diameter of the pipe
Ac	4.9087385	m^2	Cross-sectional area of the pipe
rho	8.9842472	kg/m3	Gas density
G	0.0001563	$kg/m^2/s$	Superficial mass velocity (rho * mu)
Beta0	0.015977		
alpha	9.872E-10		

Parameter	Value	Units	Description
FA0	20.9151	mols/s	Initial feed rate of species A
FB0	2.20E-02	mols/s	Initial feed rate of species B
FC0	1.19E+00	mols/s	Initial feed rate of species C
FI	1761.5853	mols/s	Feed Rate of inert species
FT0	1783.7168	mols/s	Total feed rate
sigma1	0	-	
sigma2	-0.5	-	
yB0	1.234E-05	-	
yC0	0.0006696	-	
eps1	0	-	
eps2	-0.000335	-	
kprime1	6.44E-05	1/m3	
kprime2	1.32E-03	1/m3	

*All values in orange cells calculated using Aspen HYSIS™

Parameter	Value	Units	Description
W	97500.00	kg	Weight of the catalyst
X	0.9981281		Conversion RXN 1
Y	1		Conversion RXN 2
y	0.9999519		P/P0
z	10.54	m	Length down the packed bed of pipe
	12.00	m	To Ensure full conversion
Vol	58.904862	m3	Volume of the Reactor

Zinc-Oxide Fixed Bed Reactor

Zinc Oxide Pellet Specifications and Physical Properties

Parameter	Value	Unit	
ρ_p	3140	kg/m3	Density of the Solid Particles
rho b	2190	kg/m3	Bulk Density
dp	4	mm	Particle Size of ZnO
phi	0.40	void fraction	Lee et al., 1984
	0.40	Pick up capacity by weight‡	

Annual Plant Operation 2920 hrs/yr*

‡

*Given in the problem statement

Feeds of species to be removed from Aspen HYSIS™

Species	mol/s	MW (S or Cl)	g/s Species to be Removed	kg/hr
H2S	2.20E-02	32.065	0.706	2.541
HCl	1.19E+00	35.453	84.687	304.872

Calculated Parameter	Value	Unit
Mass to be removed	307.4123	kg/hr
In a year of operation	897643.9	kg
Mass of ZnO need in one year	2244110	kg
Mass of ZnO in three years	6732329	kg
	6732.329	tonnes

Reactor Specifications

Parameter	Value	Units	
Vol	58.90486225	m^3	Total Volume
L	12	m	Length of a single column
D	2.5	m	Diameter of the column
H	12	m	

After consulting the literature it was decided that two columns in sequence will house the dechlorination and desulfurization unit processes. This makes it easier to change out the catalyst since you need the unit process to be offline for approximately 24 hrs

Pressure Rating	Construction Material	units (x)	min	max	ce
5000 kPa	Nickel alloy	Vertical height of column, m	7.0	50	500

Cost Equation, where y is the purchase cost in dollars for a CE of 500

$$y = [-150.794057377049x^2 + 152273.30942623x + 736512.55122950800]\left(\frac{556}{500}\right)\left(\frac{D}{4}\right)^{0.6}$$

Cost Eq	$1,492,518.41	For a single unit

Amount of Catalyst Needed Over Three Years and Lifetime of Plant

Mass of ZnO over three years	6732.329413	tonnes
Price of ZnO pellets*	$ 0.20	ZnO/kg

* The cost of the low-purity ZnO catalyst is given in the problem statement

C_{ZnO}	$1,346,465.88	Cost for three years of catalyst w/o replacing
	$6,732,329.41	Cost of catalyst with replacing over the lifetime of the plant

Compressor

According to hueristic 36 on p177, the maximum compression ratio that a compressor can achieve in a single stage is ~ 4.

Inlet P	35	bar
Outlet P	80	bar

Absolute pressures

atmospheric P	1.01325	bar
Inlet P	36.01325	bar abs
Outlet P	81.01325	bar abs

compression ratio	2.24954	1.12477

This suggests that we can use a single stage compressor to achieve our desired pressure increase.
According to page 169 however, our outlet temperature must not exceed 375 F.

Inlet Temp	703.3327	R	Found with aspen plus
k	1.402	unitless	Cp/Cv found with aspen hysys
a	0.286733	(k-1)/k	
Outlet temp	887.3967	R	
	427.7267	F	

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^\wedge a$$

In order to protect the compressor from damage and excessive heat, a maximum output temperature of 375 F is selected between stages.
Here, we are above that outlet temp, so we need to use a multi stage compressor.
To design our compressor, we split our pressure increase in half to ensure equal compression ratios, and make sure that our temperatures stay within our limits

SCFM	1.37E+07	Standard cubic feet per minute at 60 F and 1 atm obtained with hysys

Stage 1 calculations

Inlet P	36.01325	bar abs
Outlet P	54.01	bar abs
Compression Ratic	1.50	
Inlet Temp	703.3327	R
k	1.402	unitless
a	0.286733	(k-1)/k
Outlet temp	790.004	R
	330.334	F
THp	508247.2	Theoretical Adiabatic horsepower

$$THp = SCFM \frac{T_1}{8130a}\left[\left(\frac{P_2}{P_1}\right)^a - 1\right]$$

Between stage 1 and stage 2, there is a cooler. To prevent damage to the next stage, we must ensure that the stream remains in the vapor phase.

Bubble point	~148	F	Bubble point of the stream attained using HYSYS

To be safe, we set our cooler target temperature slightly above this at 150 F

Stage 2 calculations

Inlet P	54.01	bar abs
Outlet P	81.01325	bar abs
compression Ratio	1.50	
Inlet Temp	609.67	R
k	1.402	unitless
a	0.286733	(k-1)/k
Outlet temp	684.8309	R
	225.1609	F
THp	440749.6	Theoretical Adiabatic horsepower

$$THp = SCFM\frac{T_1}{8130a}\left[\left(\frac{P_2}{P_1}\right)^a - 1\right]$$

om Hand calculatio	Stage 1	Stage 2	Units
Inlet T	243.6627	150	F
Outlet T	330.334	225.1609	F
Inlet P	36.01325	54.01	Bar (abs)
Outlet P	54.01	81.01325	Bar (abs)
Compression Ratio	1.50	1.50	
THp	508247.2	440749.6	HP
Total Hp	948996.8		

From Aspen	Stage 1	Stage 2	Units
Inlet T	363.9681	52.91503	F
Outlet T	255.8853	80	F
Inlet P	36.01325	53.92828	Bar (abs)
Outlet P	53.92828	81.01325	Bar (abs)
Compression Ratio	1.511858	1.515808	
HP	11213.31	9763.073	HP
Total Hp	20976.38		

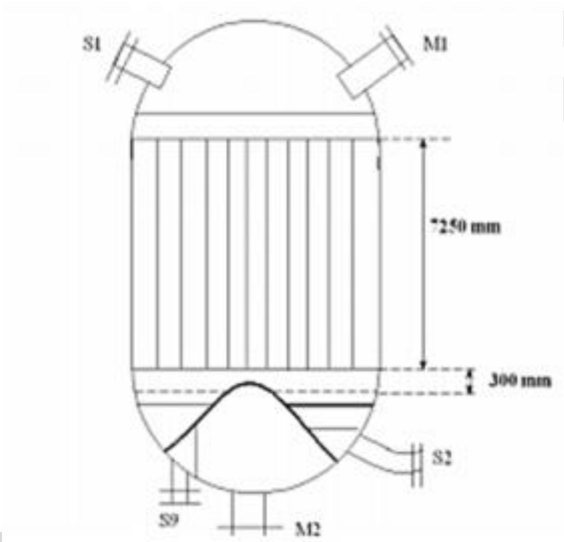
NOTE THAT ACTUAL HORSE POWER IS VERY DIFFERENT FROM THEORETICAL ADIABATIC HORSEPOWER.

Methanol Reactor

Methanol Reactor Parameters

Parameter	Value	Units	
D_t	44.5	mm	Tube inner diameter
D_0	48.5	mm	Tube outer diameter
N	4801		Number of tubes
z	7260	mm	Tube length
T0	225	˚C	Tube inlet temperature
Ts	250	˚C	Shell steam temperature
Dp	6	mm	Catalyst diameter
εB	0.4	Φ	Bed Porosity
SA	80	m^2/g	Specific surface area
pB	1100	kg/m^3	Catalyst density
Ft	40789	kmol/h	Feed flowrate
	11330.28	mol/s	
P	82	bar	Inlet Pressure

Lurgi Type Methanol Reactor diagram



Methanol Reactor Parameters

Parameter	Value	Units				
D_t	44.5	mm	Tube inner diameter			
D_0	48.5	mm	Tube outer diameter		104	
z	7260	mm	Tube length	A		4683.465
T0	270	˚C	Tube inlet temperature₮			923.7264
Ts	250	˚C	Shell steam temperature			3759.739
Dp	6	mm	Catalyst diameter			2.035093
εB	0.4	Φ	Bed Porosity			
SA	80	m^2/g	Specific surface area			
pB	1100	kg/m^3	Catalyst density			
P	80	bar	Inlet Pressure₮			

₮ Reactor conditions provided in problem statement

Ft	4.22E+03	mol/s	Feed flowrate*

*Feed flow rate into methanol reactor from ASPEN Plus™

In order to size methanol reactor, we can compare the feed molar flow rates to give us the number of tubes required for the process

Ratio	0.45769		Flow rate process/Flow rate simulation study
	2197		
N	2636.4		Number of tubes
Ac	1847.453	mm2	
	0.001847	m2	
N*Ac	4.870625	m2	
	9.912176		

Catalyst Required

Parameter	Value	Units	
V	17.86114	m3	Volume of catalyst required
W	19647.25	kg	Weight of catalyst required

Lurgi Type Methanol Reactor Costing

L	10.89	m	vessel length
D	9.91	m	vessel diameter

Cost	$ 1,380,737.41

$$C_p = \$17640 * D^{1.066} L^{0.802}$$

Catalyst

W		19647.2496	kg
Price	$	10.00	per kg

Cost	$ 196,472.50

Vapor-Liquid Flash Separator

V-L Separator Sizing

Pressure

35 Bar
507.85 psig

Inlet Vapor Flow Rate, Q	2.32E+05 ft^3/hr
	6.44E+01 ft^3/sec

Outlet Liquid Flow Rate, Q_L	2.70E+03 ft^3/hr
	7.50E-01 ft^3/sec

Vmax Calculation

Souder-Brown Equation

$$Vmax = K\left[\frac{(d_L - d_V)}{d_V}\right]^{0.5}$$

k	0.35
d_L	47.35 lb/ft^3
d_V	0.737 lb/ft^3
Vmax	2.783478 ft/sec

Area Calculation

$$Q = VmaxA$$

A	2.31E+01 ft^2

Diameter Calculation

$$A = \pi\left(\frac{D}{2}\right)^2$$

D 5.43 ft

Residence Time, τ

5 min
300 sec

Liquid Volume %

50%

$$Tank\ Volume = \frac{Q_L \tau}{Liquid\ Volume\ \%}$$

Tank Volume

450.10 ft^3

$$\text{Tank Volume} = \pi\left(\frac{D}{2}\right)^2 H$$

Diameter, D

5.43 ft

Height, H

19.5 ft

D:H Ratio

0.278811

V-L Separator Costing

Use costing Equations for a vertical pressure vessel (Seider pg 574)

Seider considerations	
CE	500
Material	C.S

Equipment Design Specs			
Temperature	122 F		
Pressure, P0	507.85 psig		
Volume	503.3 ft^3		
Diameter	5.43 ft	65.12747941 in	
Height	19.46585 ft	233.5901652 in	

Platform and Ladder Cost

$$Cpl = 361.8(Di)^{0.73960}(L)^{0.70684}$$ Seider eq. 22.56

Assumptions

3<Di<21 ft

12<H<40 ft

Cpl
10305.67 Dollars

Design Pressure, Pd

$$Pd = \exp(0.60608 + 0.91615\ln(P0) + 0.0015655(\ln(P0))^2)$$ Seider eq. 22.61

Assumptions

10<P0<1000 psig

Pd
586.77 psig

Vessel Wall Thickness, tp

$$tp = \frac{PdDi}{2SE - 1.2Pd}$$ Seider eq. 22.6

Weld Efficiency, E	0.85	
Max Allowable Stress, S	15000 psi	Seider pg. 575

tp
1.54 in

Vessel Weight, W

$$W = \Pi * (Di + tp)(L + 0.8Di)\,tp\rho$$ Seider eq. 22.59

ρ(carbon steel) 0.284 lb/in^3

W
26176.98 lb

Vessel Cost

$$Cv = \exp\left(7.0132 + 0.18255\ln(w) + 0.04333(\ln(w))^2\right)$$ Seider eq. 22.54

Assumptions
4200<W<1000000 lbs

Cv
630401.36 dollars

Vessel Base Cost, Cp (Includes Ladders/Platforms, Material of Construction, and Inflation)

$$Cp = (FmCv + Cpl)\frac{I}{Ibase}$$ Seider eq. 22.52

Fm S.S	1.7	Seider table 22.26
Fm C.S	1	
Fm	1.7	
I	556	
Ibase	500	

Cp
1203170.63 dollars

Storage Tank Sizing and Costing

Raw Methanol Storage Tank

Inlet Flow, Q	67.12 m^3/hr
Upstream Process Time, tu	8 hrs
Downstream Process Time, td	24 hrs
Residence Time, τ	16 hrs
Liq. Vol %	60%
V	1789.867 m^3

$$\boxed{\tau = td\text{-}tu}$$

$$\boxed{V = \frac{Q\tau}{Liq.Vol\,\%}}$$

Raw Methanol Storage Tank Pricing

Use Seider Table 22.32 (pg. 595) for pricing of a spherical storage tank (0-30 psig)

P	14.7 psig	
V	1789.867 m^3	472524.8 gal

Seider Assumptions

0<P<30 psig

10,000<V< gal

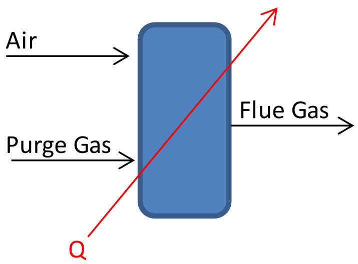
CE	500

$$\boxed{Cp = 60V^{0.72}}$$

Cp	730696.4 dollars
C_i	812534.4 dollars

Purge Gas Pyrolysis Furnace

Fired Heater Sizing



Purge Gas (H)	-1.47E+06 BTU/hr
Air (H)	-2.12E+05 BTU/hr
Hin (total)	-1.68E+06 BTU/hr
Hout (Flue Gas)	2.08E+06 BTU/hr

Use heuristic 30 and set flue gas temp to 2,000F in Aspen HYSIS™

$Q = \Delta H$ = Hout-Hin

Q	3.76E+06 BTU/hr

Fired Heater Costing

Q	3.76E+06 BTU/hr

Use Seider table 22.32 (pg. 592) for Fired heaters for specific purposes (Pyrolysis furnace)

Cp = $0.0.65Q^{0.81}$

Assumptions

Q is heat absorbed in BTU/hr

Valid for 10-500 million BTU/hr

Cbase	$137,781.07

Actual energy is less than 10 million BTU/hr so use 0.6 factor for economy of size

$$Cost = Cp\left(\frac{Q}{Qbase}\right)^{0.6}$$

Cbactual	$76,661.85

Account for inflation with CE factors

$$C_i = Cost\frac{I}{Ibase}$$

C_i	$85,247.98

C_p	$144,921.57

Pumps

Pump-1

Pump-1 Size Calcs

Q			
803.8 ft^3/hr	101 gpm		User defined input in Aspen Plus

Theoretical Pump Head

$$ha = \frac{\Delta P}{\Upsilon}$$ Munson eq. 12.20

Inlet pressure	14.7 psia	
Discharge Pressure	507.5 psia	
ΔP	492.8 psia	
ϒ	62.4 lb/ft^3	0.036111 lb/in^3

Head, ha	
1137.230769 ft	493.5581538 psia

$$NPSH_A = P_{inlet} - P^*$$

P*	0.4597 psia	calculated via Aspen Hysys (Vapor Pressure Calculation)
Pinlet	14.7 psia	

NPSHA	14.2403 psia

Pump-1 Cost

Use Seider pg. 560-562 for pricing of centrifugal pumps

Q	101 gpm
H	1137.231 ft

Size Factor, S

$S = Q(H)^{0.5}$ Seider eq. 22.13

S	3396.796

Base Cost, Cb

$Cb = \exp\{9.7171 - 0.6019[\ln(S)] + 0.0519[\ln(S)]^2$ Seider eq. 22.14

Cb	
	3843.83 dollars

Purchase cost, Cp

$Cp = F_T F_M C_B$ Seider eq. 22.15

FT	1	Table 22.20
FM	2	Table 22.21 (S.S)

Cp		CE(556/500)
	7687.66 dollars	8548.676423

Pump-2

Pump-1 Size Calcs

Q		
655 gpm	655 gpm	User defined input in Aspen Plus

Theoretical Pump Head

$$ha = \frac{\Delta P}{\Upsilon}$$ Munson eq. 12.20

Inlet pressure	14.7 psia	
Discharge Pressure	507.5 psia	
ΔP	492.8 psia	
ϒ	62.4 lb/ft^3	0.036111 lb/in^3

Head, ha	
1137.230769 ft	493.5581538 psia

$$NPSH_A = P_{inlet} - P^*$$

P*	0.4597 psia	calculated via Aspen Hysys (Vapor Pressure Calculation)
Pinlet	14.7 psia	

NPSHA	14.2403 psia

Pump-2 Cost

Use Seider pg. 560-562 for pricing of centrifugal pumps

Q	655 gpm
H	1137.231 ft

Size Factor, S

$S = Q(H)^{0.5}$ Seider eq. 22.13

S	22083.41

Base Cost, Cb

$Cb = \exp\{9.7171 - 0.6019[\ln(S)] + 0.0519[\ln(S)]^2$ Seider eq. 22.14

Cb

7253.41 dollars

Purchase cost, Cp

$Cp = F_T F_M C_B$ Seider eq. 22.15

FT	1	Table 22.20
FM	2	Table 22.21 (S.S)

Cp

14506.81 dollars

CE(556/500)

16131.57318

Pump-3

Pump-1 Size Calcs

Q

115.1 gpm User defined input in Aspen Plus

Theoretical Pump Head

$$ha = \frac{\Delta P}{\Upsilon}$$ Munson eq. 12.20

Inlet pressure	14.7 psia		
Discharge Pressure	44.1 psia		
ΔP	29.4 psia		
ϒ	62.4 lb/ft^3	0.036111	lb/in^3

Head, ha

67.84615385 ft 29.44523077 psia

$$NPSH_A = P_{inlet} - P^*$$

P*	0.4597 psia	calculated via Aspen Hysys (Vapor Pressure Calculation)
Pinlet	14.7 psia	

NPSHA 14.2403 psia

Pump-3 Cost

Use Seider pg. 560-562 for pricing of centrifugal pumps

Q	115 gpm
H	67.84615 ft

Size Factor, S

$S = Q(H)^{0.5}$ Seider eq. 22.13

S	948.0646

Base Cost, Cb

$Cb = \exp\{9.7171 - 0.6019[\ln(S)] + 0.0519[\ln(S)]^2$ Seider eq. 22.14

Cb
3071.27 dollars

Purchase cost, Cp

$Cp = F_T F_M C_B$ Seider eq. 22.15

FT	1	Table 22.20
FM	2	Table 22.21 (S.S)

Cp	CE(556/500)
6142.54 dollars	6830.504308

Total Pump Costs

Total Pump Costs

$$Total\ Pump\ Cost = (C_{P1} + C_{P2} + C_{P3})\left(\frac{I}{I_{base}}\right)$$

I	556
Ibase	500

Total pump cost
31510.75 dollars

Distillation Column

Valve Tray Distillation

$$D_T = \left[\frac{4G}{(fU_f)\,\pi\,[1-(A_d/A_T)]\rho_G}\right]^{1/2}$$

$$C = C_{SB}\,F_{ST}\,F_F\,F_{HA}$$

Where: G = mass flow rate of vapor (e.g. kg/s)
A_d = downcomer area (e.g. m²)
ρ_g = vapor density (e.g. kg/m³)
A_T = tower inside cross-sectional area (e.g. m²)
f = fraction of the vapor flooding velocity (~ 0.75 to 0.85)
U_f = vapor flooding velocity (e.g. m/s)
D_T = tower diameter (e.g. m)

$$U_f = C[(\rho_L - \rho_G)/\rho_G]^{1/2}$$

ρ_L = liquid density (e.g. kg/m³)
C = Empirical Capacity Parameter

F_{ST} = surface tension factor = $(\sigma/20)^{0.20}$
where σ is surface tension in (dyne/cm)
F_F = foam factor (=1 typical for distillation systems;
= 0.5 to 0.75 for foaming systems)
F_{HA} = hole factor (=1 for valve and bubble-cap trays;
=1 for sieve trays for $(A_h/A_a > 0.10)$
$= [5(A_h/A_a) + 0.5)]$ for $0.06 < (A_h/A_a) < 0.1)$
where A_h = hole area of tray
A_a = active area of tray = $(A_T - 2A_d)$
where bubbling occurs

Plate Spacing			
18 in	1.5 ft	0.5112 m	
Csb			
0.3 ft/s	0.10224 m/s		
σ			
27.855 dyne/cm			
Fst			
1.068500263			
Ff			
1			
FHA			
1			
C			
0.109243467 m/s			
L			
3.58E+04 kg/hr	9.94E+00 kg/s		

G	
7.00E+04 kg/hr	1.94E+01 kg/s
pg	
2.445 kg/m3	
pl	
733.83 kg/m3	
Flg	
0.029496	
Ad/At	
0.1	
Uf	
1.889422	
f	
0.8	

$$U_f = C[(\rho_L - \rho_G)/\rho_G]^{1/2}$$

ρ_L = liquid density (e.g. kg/m³)
C = Empirical Capacity Parameter

$$TowerHeight = N * Tray\ Spacing$$

Dtower
2.728932 m

Tower Height
8.1792 m

Tray Calculations

	Distillation Streams		
Property	**Feed**	**Distillate**	**Bottoms**
Klk	1.17	1	1.523
Khk	0.3	0.2238	0.4767
xlk	0.9654	0.9997	0.5
xhk	0.0346	0.0003	0.5
Flow Rate (kmol/hr)	623	601.5	21.5

$$N_{min} = \frac{\ln[(x_{LK}/x_{HK})_D (x_{HK}/x_{LK})_B]}{\ln[\alpha_{LK/HK}]_{av}}$$

where x_{LK} = mole fraction of light key component
x_{HK} = mole fraction of heavy key component
$\alpha_{LK/HK\ av}$ = avg geometric relative volatility
$= [(\alpha_{LK/HK})_D (\alpha_{LK/HK})_B]^{1/2}$ where $(\alpha_{LK/HK})_D = K_{LK}/K_{HK}$
D = distillate, B = bottoms products

http://pubs.acs.org/doi/pdfplus/10.1021/ie030407n

alpha average

3.778307798

Nmin

6.102138753 stages

Nmin rounded

7 stages

$$\sum_{i=1}^{n} \frac{(\alpha_i)(x_{F,i})}{(\alpha_i - \Theta)} = 1 - q$$

(solve for Θ by trial and error)

n = number of individual components in the feed
α_i = avg geometric relative volatility of component i in the mixture relative to the heavy key component
$x_{F,i}$ = mole fraction of component i in the feed
q = moles of saturated liquid on the feed tray per mole of feed
Θ lies between the relative volatilities of the two key components

θ 1.026106684 solve for θ using excel solver function
q 1 (sat'd liquid)

component	alpha	(alpha)(Xf)/(alpha-theta)
methanol	3.778307798	1.325331325
water	1	-1.325331066
sum		2.58811E-07

$$R_{min} + 1 = \sum_{i=1}^{n} \frac{(\alpha_i)(x_{D,i})}{(\alpha_i - \Theta)}$$

$x_{D,i}$ = mole fraction of component i in the distillate

component	alpha	Xdi	(alpha)(xd)/(alpha-theta)
methanol	3.778307798	0.9997	1.372419438
water	1	0	0
		sum	1.372419438
		Rmin	0.372419438
		R	0.558629157

$$\frac{N - N_{min}}{N + 1} = 0.75\,[\,1 - (\frac{R - R_{min}}{R + 1})^{0.566}]$$

N-Nmin/N+1	0.524684967	
N	15.83094254	stages
Nactual	16	stages

$$\ln(N_B/N_D) = 0.206\,\ln\{(B/D)\ (x_{HK}/x_{LK})_F\ [(x_{LK})_B/(x_{HK})_D]^2\}$$

B = molar flow rate of bottoms
D = molar flow rate of distillate
N_D = number of equilibrium stages above feed tray
N_B = number of equilibrium stages below feed tray

ln(Nb/Nd)	1.684482469	
Nb/Nd	5.389660894	
Nd	2.504045248	stages
optimum feed	14	stage
Nb+Nd	16	stages

Distillation Tower Pricing

Use costing Equations for a vertical pressure vessel (Seider pg 574)

Seider considerations	
CE	500
Material	C.S

Equipment Design Specs

Variable	Value	Units
Temperature	122	F
Pressure, P0	40	psig
Diameter	2.728932087	m
	8.950897244	ft
	107.4107669	in
Height	8.1792	m
	26.827776	ft
	321.933312	in

Platform and Ladder Cost

$$\boxed{Cpl = 361.8(Di)^{0.73960}(L)^{0.70684}}$$

Seider eq. 22.56

Assumptions

3<Di<21 ft

12<H<40 ft

Cpl	$ 18,717.59

Design Pressure, Pd

$$\boxed{Pd = \exp(0.60608 + 0.91615\ln(P0) + 0.0015655(\ln(P0))^2)}$$

Seider eq. 22.61

Assumptions

10<P0<1000 psig

Pd	54.97892733 psig

Vessel Wall Thickness, tp

$$\boxed{tp = \frac{PdDi}{2SE - 1.2Pd}}$$

Seider eq. 22.6

Weld Efficiency, E	0.85	
Max Allowable Stress, S	15000 psi	Seider pg. 575

tp	0.232182232 in

Vessel Weight, W

$$\boxed{W = \Pi * (Di + tp)(L + 0.8Di)\,tp\rho}$$

Seider eq. 22.59

ρ(carbon steel)	0.284 lb/in^3

W	9090.247801 lb

Vessel Cost

$$Cv = \exp(7.0132 + 0.18255\ln(w) + 0.04333(\ln(w))^2)$$

Seider eq. 22.54

Assumptions

4200<W<1000000 lbs

Cv	$ 214,721.69

Vessel Base Cost, Cp (Includes Ladders/Platforms, Material of Construction)

$$Cp = (FmCv + Cpl)$$

Seider eq. 22.52

Fm S.S	1.7	Seider table 22.26
Fm C.S	1	
Fm	1.7	

Cp	$ 383,744.46

Base Cost of Tower Trays

$$Cbt = 468\exp(0.1739D)$$

Seider eq. 22.67

Cbt	$ 2,219.48

Installed Cost of Trays

$$Ct = NtFntFttFtmCbt$$

Seider eq. 22.66

Nt	16	stages
Fnt	1.175713066	pg.577
Ftt	1.18	pg.577

$$Ftm = 1.401 + 0.0724D$$

Ftm	2.05	ft

$$F_{NT} = \frac{2.25}{1.0414^{NT}}$$

Ct	$ 100,950.05

Total Cost of Installed Distillation Tower (Includes inflation)

$$Total\ Tower\ Cost = (Cp+Ct)\left(\frac{I}{Ibase}\right)$$

I	556
Ibase	500

Total Tower Cost	$ 538,980.30

Distillation Condenser (1-2 Heat Exchanger) Sizing

From Hysys Sim		
Qreboiler	3.09E+07	BTU/hr
T Cold-In	90	F
T Cold-Out	146	F
T Hot-In	190.1	F
T Hot-Out	166	F

Cooling water provided at 90 deg F and 1 atm

Heuristic 26

cryogenic: 1-to-2°F; 10°F or less for temperatures < ambient
ambient: 10°F; 20°F for ambient to 300°F
high temperature: ~100°F

$$\Delta T_{LM} = \frac{\Delta T_1 - \Delta T_2}{ln\left(\Delta T_1 / \Delta T_2\right)} \qquad R = \frac{T_{Hin} - T_{Hout}}{T_{Cout} - T_{Cin}} \qquad S = \frac{T_{Cout} - T_{Cin}}{T_{Hin} - T_{Cin}}$$

ΔT1	44.1	F
ΔT2	76	F
ΔTlm	58.61	F
R	0.43	
S	0.56	

1-2 heat exchanger

$$F_T = \frac{\sqrt{R^2+1}\cdot ln\left[\dfrac{1-S}{1-RS}\right]}{(R-1)\cdot ln\left[\dfrac{2-S\left(R+1-\sqrt{R^2+1}\right)}{2-S\left(R+1+\sqrt{R^2+1}\right)}\right]}$$

Sqrt(R^2+1) 1.088672

Ft	0.93

$0.85 \le F_T \le 1$ desirable

Use a 1-2 heat exchanger since Ft is satisfied for 1-2 heat exchanger requirements

$$\Delta T_m = F_T \Delta T_{LM}$$

ΔTm	54.47994 F	73.5

Estimate U from Seider Table 18.5, For Low Boiling Hydrocarbons and water (U= 80-200)

U	140 BTU/(F-Ft^2-hr)

$$Q = UA\Delta T_m$$

Area	4044.74 ft^2

Distillation Condenser (1-2 Heat Exchanger) Pricing

Use Seider Eqautions for a U-tube Shell-and-tube heat exchanger section 22.5

Seider Considerations	
CE	500
Material	S.S/S.S

$$Cb = \exp\{11.147 - 0.9186[\ln(A)] + 0.09790[\ln(A)]^2\}$$

Seider eq. 22.41

For P<100 psig

150<A<12000 ft^2

P	14.7 psig
A	4044.74 ft^2

Cb
28871.44 dollars

$$Cp = FpFmFlCb$$

Seider eq. 22.43

Fp	1
Fl	1.05 Seider pg. 571

$$Fm = a + \left(\frac{A}{100}\right)^b$$

Seider eq. 22.44

Material	**a**	**b**
S.S/S.S	2.7	0.07

Fm	3.995634

Cp
121127.68 dollars

Distillation Re-boiler (1-2 Heat Exchanger) Sizing

From Hysys Sim		
Qreboiler	3.29E+07	BTU/hr
T Cold-In	266.4	F
T Cold-Out	266.8	F
T Hot-In	280.4	F
T Hot-Out	276.8	F

LPS provided at 50 psig and 280.4 F, Hot-Outlet Temp estimated using minimum approach Temp heuristic below

Heuristic 26

- cryogenic: 1-to-2°F; 10°F or less for temperatures < ambient
- ambient: 10°F; 20°F for ambient to 300°F
- high temperature: ~100°F

$$\Delta T_{LM} = \frac{\Delta T_1 - \Delta T_2}{ln\left(\Delta T_1 / \Delta T_2\right)} \qquad R = \frac{T_{Hin} - T_{Hout}}{T_{Cout} - T_{Cin}} \qquad S = \frac{T_{Cout} - T_{Cin}}{T_{Hin} - T_{Cin}}$$

ΔT1	13.6	F
ΔT2	10.4	F
ΔTlm	11.93	F
R	9.00	
S	0.03	

1-2 heat exchanger

$$F_T = \frac{\sqrt{R^2+1} \cdot ln\left[\dfrac{1-S}{1-RS}\right]}{(R-1) \cdot ln\left[\dfrac{2-S\left(R+1-\sqrt{R^2+1}\right)}{2-S\left(R+1+\sqrt{R^2+1}\right)}\right]}$$

Sqrt(R^2+1) 9.055385

Ft	1.00

$0.85 \le F_T \le 1$ desirable

Use a 1-2 heat exchanger since Ft is satisfied for 1-2 heat exchanger requirements

$$\Delta T_m = F_T \Delta T_{LM}$$

ΔTm	11.90833 F

Estimate U from Seider Table 18.5, For Low Boiling Hydrocarbons and water (U= 80-200)

U	140 BTU/(F-Ft^2-hr)

$$Q = UA\Delta T_m$$

Area	19740.09 ft^2

Distillation Re-boiler (1-2 Heat Exchanger) Costing

Use Seider Eqautions for a U-tube Shell-and-tube heat exchanger section 22.5

Seider Considerations	
CE	500
Material	S.S/S.S

$$Cb = \exp\{11.147 - 0.9186[\ln(A)] + 0.09790[\ln(A)]^2\}$$

Seider eq. 22.41

For P<100 psig
150<A<12000 ft^2

P	50	psig
A	19740.09	ft^2

Cb
113353.27 dollars

$$Cp = FpFmFlCb$$

Seider eq. 22.43

Fp	1	
Fl	1.05	Seider pg. 571

$$Fm = a + \left(\frac{A}{100}\right)^b$$

Seider eq. 22.44

Material	**a**	**b**
S.S/S.S	2.7	0.07

Fm	4.147686192

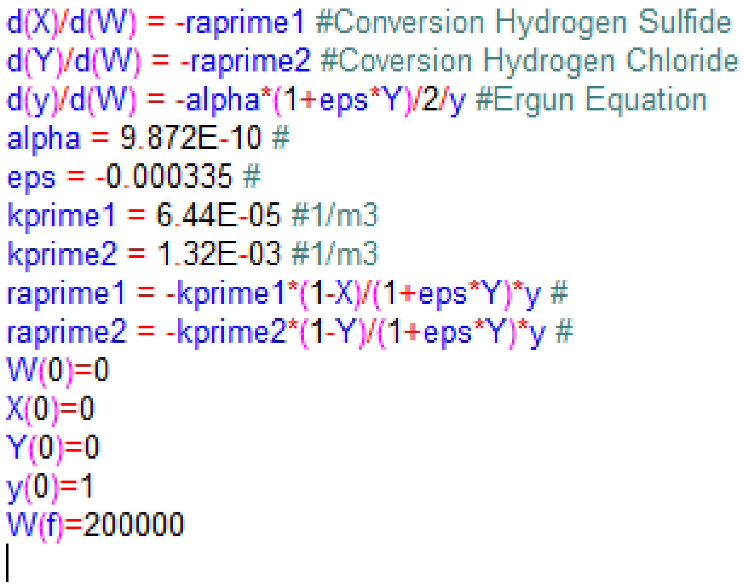
Cp
493661.49 dollars

Appendix D. Computer Process Modeling/Simulation

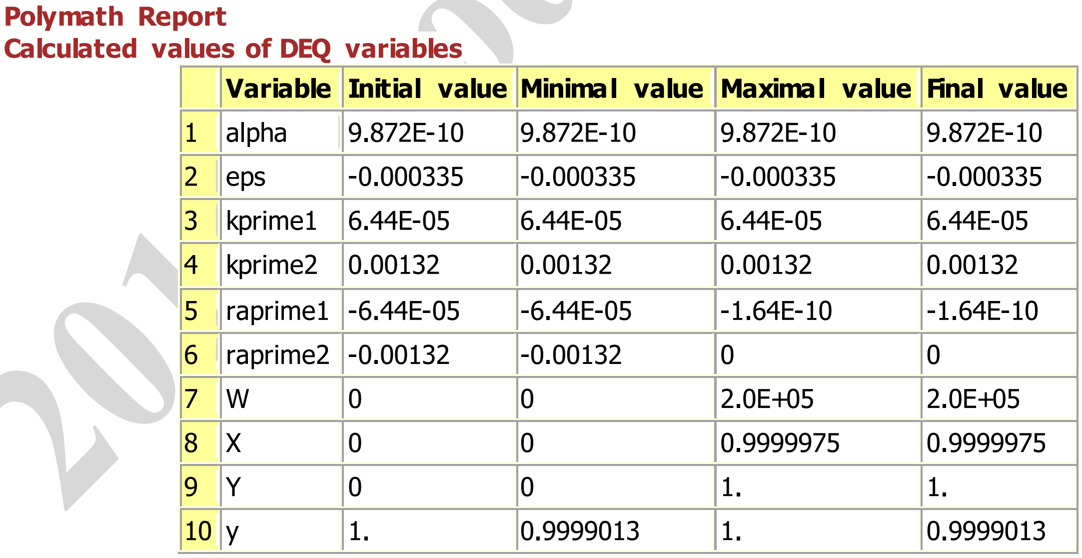
POLYMATH™

ZnO Fixed Bed Reactor

POLYMATH™ Code used to size the zinc oxide fixed bed reactor. Consult Appendix D for the detailed calculations.



```
d(X)/d(W) = -raprime1 #Conversion Hydrogen Sulfide
d(Y)/d(W) = -raprime2 #Coversion Hydrogen Chloride
d(y)/d(W) = -alpha*(1+eps*Y)/2/y #Ergun Equation
alpha = 9.872E-10 #
eps = -0.000335 #
kprime1 = 6.44E-05 #1/m3
kprime2 = 1.32E-03 #1/m3
raprime1 = -kprime1*(1-X)/(1+eps*Y)*y #
raprime2 = -kprime2*(1-Y)/(1+eps*Y)*y #
W(0)=0
X(0)=0
Y(0)=0
y(0)=1
W(f)=200000
```



Polymath Report
Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	alpha	9.872E-10	9.872E-10	9.872E-10	9.872E-10
2	eps	-0.000335	-0.000335	-0.000335	-0.000335
3	kprime1	6.44E-05	6.44E-05	6.44E-05	6.44E-05
4	kprime2	0.00132	0.00132	0.00132	0.00132
5	raprime1	-6.44E-05	-6.44E-05	-1.64E-10	-1.64E-10
6	raprime2	-0.00132	-0.00132	0	0
7	W	0	0	2.0E+05	2.0E+05
8	X	0	0	0.9999975	0.9999975
9	Y	0	0	1.	1.
10	y	1.	0.9999013	1.	0.9999013

Differential equations

1 d(X)/d(W) = -raprime1

Conversion Hydrogen Sulfide

2 d(Y)/d(W) = -raprime2

Coversion Hydrogen Chloride

3 d(y)/d(W) = -alpha*(1+eps*Y)/2/y

Ergun Equation

Explicit equations

1 alpha = 9.872E-10

2 eps = -0.000335

3 kprime1 = 6.44E-05

1/m3

4 kprime2 = 1.32E-03

1/m3

5 raprime1 = -kprime1*(1-X)/(1+eps*Y)*y

6 raprime2 = -kprime2*(1-Y)/(1+eps*Y)*y

General

Total number of equations	9
Number of differential equations	3
Number of explicit equations	6
Elapsed time	0.000 sec
Solution method	stiff
Independent variable accuracy. eps	0.00001
First stepsize guess. h1	0.0001
Minimum allowed stepsize. hmin	0.00000001
Good steps	277
Bad steps	0

Appendix E. Economic Analysis

Utility Calculations

Hourly Utility Calculations for Steam and Cooling Water

Re-boiler (Low Pressure saturated Steam provided at 50 psig)

Steam is assumed to be condensing to a saturated liquid inside heat exchanger

Equipment

Re-boiler

Properties of steam	Pressure (kPa)	Temperature (°C)	Hvapor (kJ/kg)	ΔHVap (kJ/kg)	Hliquid (kJ/kg)
Inlet Properties	344.7	147.6	2730.5	2150.5	579.7
Outlet Properties	320	136	2728	2157	570.9

$$Q = m\Delta H$$

ΔH=(Hin+ΔHVap -HLout)

Energy balances

Q	3.47E+07	kJ/hr	simulated by Aspen Hysys
ΔH	4310.1	kJ/kg	Heat added to system
m	8055.4976	kg/hr	

Condenser (Cooling Water provided at 90°F)

cooling water is assumed to meet minimum approach T for condensing meOH at condenser pressure (30psig)

Equipment

Condenser

Properties of Steam	Pressure (kPa)	Temperature (°C)	Hvapor (kJ/kg)	ΔHVap (kJ/kg)	Hliquid (kJ/kg)	Specific Volume (m^3/kg)
Inlet Properties		32.2	2632	2327	304.3	0.001
Outlet Properties		63.3	2657	2288	368.6	

$$Q = m\Delta H$$

ΔH=(HLout-HLin)

Energy balances

Q	3.25E+07	kJ/hr	simulated by Aspen Hysys
ΔH	64.3	kJ/kg	heat removed from system
m	5.05E+05	kg/hr	
Volumetric flow	5.05E+02	m^3/hr	

Interstage Cooler (Cooling water provided at 90°F)

cooling water is assumed to meet minimum approach T of 275°F from heuristic 26 and evaporating

Properties of Steam	Pressure (kPa)	Temperature (°C)	Hvapor (kJ/kg)	ΔHVap (kJ/kg)	Hliquid (kJ/kg)	Specific Volume (m^3/kg)
Inlet Properties		32.2	2632	2327	304.3	0.001
Boiling at 1atm				2257		
Outlet Properties		135	2728	2157	570.9	

$$Q = m\Delta H$$

ΔH=(HVout+ΔHvap(1atm)-Hlin)

Q	83064757	kJ/hr	simulated by Aspen Plus
ΔH	4680.7	kJ/kg	
m	17746.225	kg/hr	
Volumetric flow	17.746225	m^3/hr	

MeOH Reactor (Cooling water provided at 90°F)

cooling water is assumed to meet minimum approach T of 400°F from heuristic 26 and evaporating

Properties of Steam	Pressure (kPa)	Temperature (°C)	Hvapor (kJ/kg)	ΔHVap (kJ/kg)	Hliquid (kJ/kg)	Specific Volume (m^3/kg)
Inlet Properties		32.2	2632	2327	304.3	0.001
Boiling at 1atm				2257		
Outlet Properties		204	2792	1933	859	

$$Q = m\Delta H$$

ΔH=(HVout+ΔHvap(1atm)-Hlin)

Q	81186101	kJ/hr
ΔH	4744.7	kJ/kg
m	17110.903	kg/hr
volumetric flow	17.110903	m^3/hr

Hourly and Annual Utility Calculations for Methanol Production Process

$$Annual\ Upstream\ Duty = (Required\ hourly\ Duty)\left(\frac{8hr}{day}\right)\left(\frac{365day}{year}\right)$$

$$Annual\ Downstream\ Duty = (Required\ hourly\ Duty)\left(\frac{24hr}{day}\right)\left(\frac{365day}{year}\right)$$

Water

Equipment	Required Duty (m^3/hr)	Annual Duty (m^3)	Cost/m^3 (USD)	Annual Cost (USD)	Cost/gal MeOH (USD/gal)
Solar Reactor	22.7628	66467.376	0.19	12628.8	0.000226
Spray-Q-T	148.73	434291.6	0.019	8251.54	0.000147
interstage cooler	17.74623	51818.97802	0.019	984.5606	1.76E-05
MeOH Reactor	17.1109	49963.83647	0.019	949.3129	1.7E-05
Condenser	5.05E+02	4.43E+06	0.019	8.41E+04	0.001502
Total	711.7932	5030224.528	-	106940.2	0.00191

Electricity

Equipment	Required Duty (kW)	Annual Duty (kW-hr)	Cost/kW-hr (USD)	Annual Cost (USD)	Cost/gal MeOH (USD/gal)
Pump-1	40.11	117121.2	0.06	7027.272	0.000125
Pump-2	190.56	556435.2	0.06	33386.11	0.000596
Compressor	15642	45674640	0.06	2740478	0.048937
Fired Heater	1103	9662280	0.06	579736.8	0.010352
Pump-3	1.9	16644	0.06	998.64	1.78E-05
Total	16977.57	56027120.4	-	3361627	0.060029

Low Pressure Steam

Equipment	Required Duty (kg/hr)	Annual Duty (kg/year)	Cost/kg (USD)	Annual Cost (USD)	Cost/gal MeOH (USD/gal)
Re-boiler	8055.498	70566158.56	0.00786	554650	0.009904
Total	8055.498	70566158.56	-	554650	0.009904

Total Annual Utility costs	4023217	dollars
Total Utility Cost/gal MeOH	0.071843	USD/gal

Number of Operators Calculations

Process	Type of Process	Operators/Section	Shifts	Total
Solar	Fluid Processing	3		0
ZnO Reactor	Fluid Processing	3		0
Methanol Reactor	Fluid Processing	2		0
Liquid Product Separations*	Fluid Processing	2		0
		10	5	
			Total	50

From table 23.3

For a semi-batch process with over 1000 ton/day product

*For a continuous process with over 1000 ton/day product

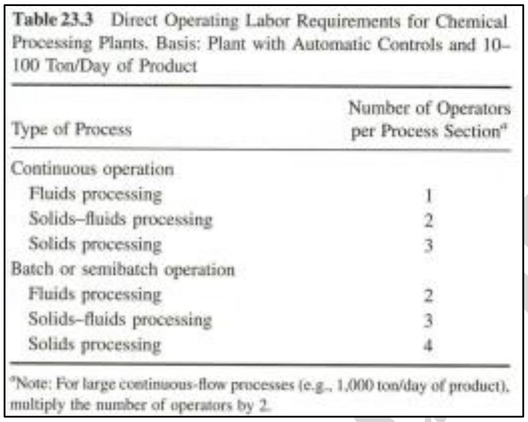


Table 23.3 Direct Operating Labor Requirements for Chemical Processing Plants. Basis: Plant with Automatic Controls and 10–100 Ton/Day of Product

Type of Process	Number of Operators per Process Section[a]
Continuous operation	
Fluids processing	1
Solids–fluids processing	2
Solids processing	3
Batch or semibatch operation	
Fluids processing	2
Solids–fluids processing	3
Solids processing	4

[a]Note: For large continuous-flow processes (e.g., 1,000 ton/day of product), multiply the number of operators by 2.

VENTURE GUIDANCE APPRAISAL

🟨 =User Input 🟦 =Calc by Computer

Title:	Methanol Production by Gassification of Biomass		Date:	1/18/11
Product	Methanol			
Units of Capacity		Gal		
Öperating Hours per Year		8,000		
Capacity:	56,000,000		Site:	US Southwest
Capacity:	100,100	Gal per Hour		

Enter cost of Land into cell B22 on Cash Flow sheet.

					Item Cost ($k)	Subtotal ($k)
Bare Module Cost (BMC)/Direct Installed Cost (DIC)						
Engineered Equipment/Purchased						
	ZnO Bed Reactor (2 Units)				1,493	
	Re-boiler				494	
	Condenser				121	
	Pyrolysis Furnace				145	
	Pumps				32	
	Storage Tank				813	
	V-L Flash Separator				1,275	
	Spray-Q-Tank				487	
	Cyclone				12	
	Compressor				10,300	
	Cutter				3,228	
	Solar Reactor				15352	
	Grinder				9,342	
Total Engineered Equipment/Purchased&Delivered					43,093	
Misc Equipment		10%			4,309	
	Subtotal/Purchased Equipment&Delivered					47,402
Field Mtl/Labor/Insulation		5%	10%	10%	12,822	
Field Erected Equipment						
Equip Fdns,Sppts, Platforms		10%			6,022	
	Installed Equipment					66,247
Factored Piping		22%			14,574	
Factored Instruments		9%			5,962	
Factored Electrical		7%			4,637	
Identified Piping						
Identified Instruments						
Identified Electrical						
	Subtotal/Direct Installed Cost					91,421

Labor/Material Split	40%	L	60%	M		
Freight, Quality Assurance, Sales Taxes	12%	of Matl			6,582	
Contractor Labor Distributives	44%	of Labor			16,090	
Subtotal (Direct Installed Cost + Indirect Freight, QA, Taxes, & Overhead)						114,093
Engg+Home Office (Additional Indirect)	15%	of Total			17,114	
Subtotal (DIC Equipment Calculated from Bare Module using PE)						131,207
PE with FBM factors	PE	FBM				
Equipment at Bare Module Level	Cost	Factor				
Heliostats / Tower	74899	1			74,899	
Secondary	778	1			778	
Land	275	1			275	
Lurgi Methanol Reactor	1577	1			1,577	
Distillation Column	539	1			539	
Subtotal (DIC from Total Bare Module Cost w/FBM Factors)					78,068	
Misc. Equipment	10%				7,807	
Subtotal (DIC Equipment from Bare Module Costs)						217,082
Subtotal (DIC Equipment Costs)..						217,082
Buildings, Structure	5%				10,854	
Subtotal						227,936
Power, General, & Services (PG&S)	2%				4,559	
Dismantling & Rearranging (D&R)	2%				4,559	
Site Development	4%				9,117	
Subtotal (DPI)						246,171
Contingency	15%				36,926	
Subtotal						283,097
Working Conditions		of Labor				
Net Total						283,097
Minor Changes						
Direct total						283,097
Field Indirects		of Total				
Spares & Portables						
Total Equipment						283,097
						EQUIP
Total (Current $$, USGC)						283,097
Site Factor	100%	of USGC Total				283,097
Inflation	1.9%	for	2.0	yrs		293,957
Scope Growth						
Total Project-Level Cost						293,957
			SAY			294,000
GRAND TOTAL (TPI)					$	**294,000** k

Working Capital

WORKING CAPITAL

Start-up Raw Materials Inventory From Table 4.2

	Quantity	Units	Price			
Methane	528,000,000	SCF	0.00	/SCF	$2,112	k
Biomass	18,732	metric ton	60.00	/metric ton	$1,124	k
ZnO Catalyst	6,732,329	kg	0.20	/kg	$1,346	k
Water	16,387	m^3	0.19	/m3	$3	k
MeOH Catalyst	1,964,700	kg	10.00	/kg	$19,647	k
				Total	$24,232	k

Start-up Spare Parts: 2.5% of Investment $7,350 k

TOTAL WORKING CAPITAL... $31,582

Site factor table	
US Gulf Coast	1.00
US Southwest	0.95
US Northeast	1.10
US Midwest	1.15
US West Coast	1.25
Western Europe	1.20
Mexico	0.95
Japan	1.15
Pacific Rim	1.00
India	0.85

Operating Cost Estimate: Variable Cost

OPERATING COST ESTIMATE
VARIABLE COST

🟨 =USER INPUT 🟦 =CALC BY COMPUTER

PRODUCT: Methanol

ANNUAL CAPACITY: 56,000,000 Gal per Year

INGREDIENTS:	UNIT OF MEASURE	COST PER UNIT ($)	UNITS OF INGRED/ Gal PRODUCT	COST PER Gal of PRODUCT ($)		
Methane	SCF	0.004	35.00000	0.140		
Biomass	metric ton	60.00	0.0012	0.074		
Process Water	m^3	0.19	0.00108	0.000		
SUBTOTAL INGREDIENTS					0.215	
UTILITIES:						
Cooling water	m^3	0.019	0.080948421	0.002		
Electricity	kW-hr	0.06	0.914	0.055		
LP STEAM	kg	0.00786	1.150785365	0.009		
Waste treatment	kg	0.31	0.133809524	0.041		
SUBTOTAL UTILITIES					0.107	
CATALYSTS & CHEMICALS						
ZnO	kg	0.2	0.032	0.006		
SUBTOTAL CATALYSTS & CHEMICALS					0.006	
PACKAGING MATERIALS						
PACKAGING LABOR						
BYPRODUCT CREDIT	gal	0.4	1		-0.400	
OTHER VARIABLE COSTS						
TOTAL VARIABLE COST					-$0.072	per Gal
					($4,041)	k per Year

Operating Cost Estimate: Fixed Cost

OPERATING COST ESTIMATE
FIXED COST

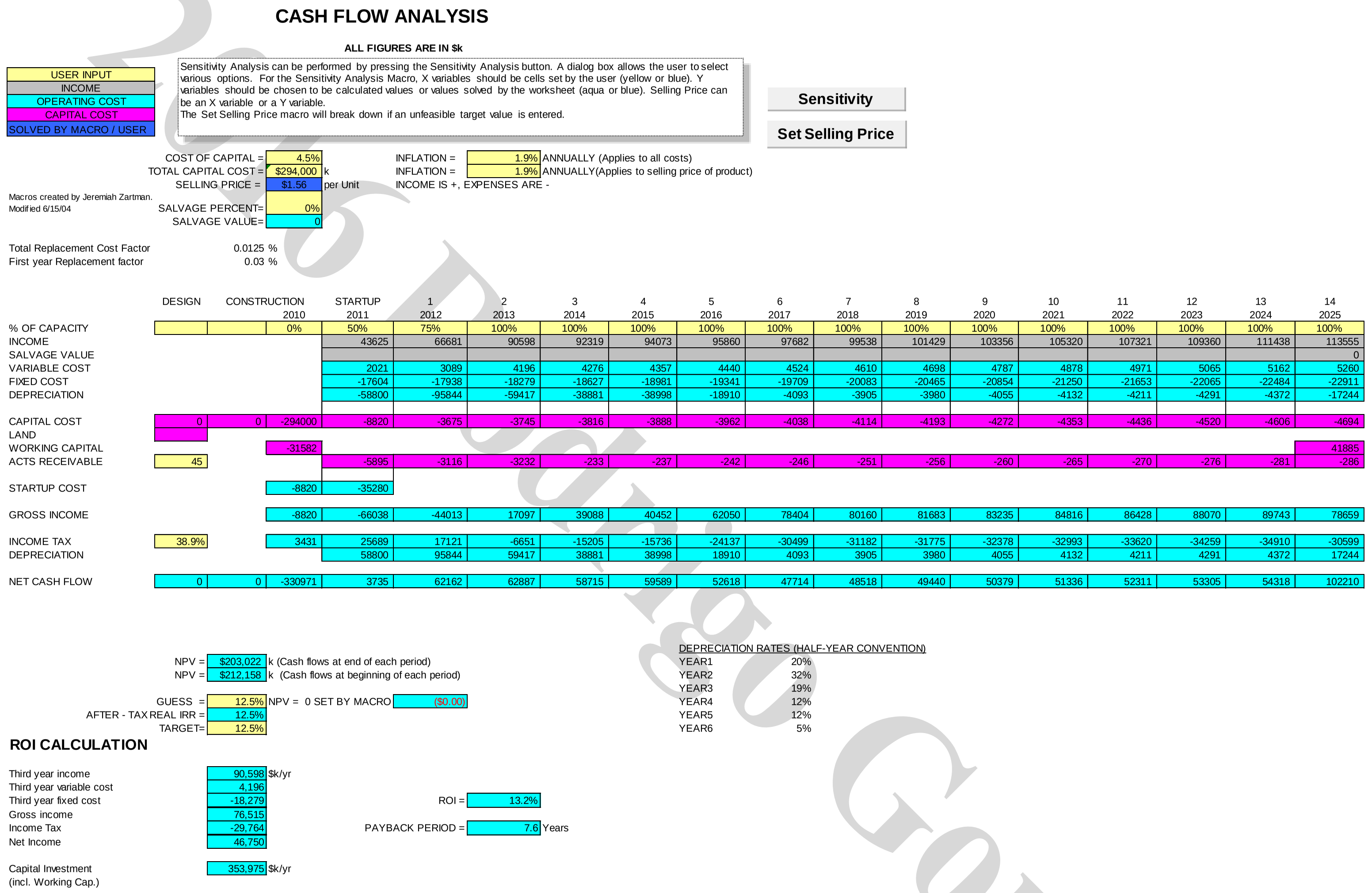
🟨 =USER INPUT 🟦 =CALC BY COMPUTER

PRODUCT:	Vinyl Chloride			
ANNUAL AnnCap:	56,000,000	Gal per Year		
TOTAL INVESTMENT (TPI):	$294,000	k		
OPERATING LABOR & BENEFITS:			ANNUAL COST ($k/yr)	
NO. of OPERATORS:	50			
ANNUAL WAGES	$104	k PER OPERATOR	5,200	
EMPL. BENEFITS @		of WAGES		
OPERATING SUPERVISION @		of WAGES		
SUBTOTAL OPERATING LABOR:				5,200
OPERATING SUPPLIES:		of WAGES		
MAINTENANCE:				
TOTAL MAINTENANCE @		OF INVESTMENT		
MAINTENANCE LABOR@		of TOTAL MAINT.		
MAINTENANCE MATERIAL @		of TOTAL MAINT.		
OVERHEAD:				
GEN. OH @		of (OPR. WAGES + MAINT LABOR + OPR. SUPRV.)		
LAB &TECHNICAL SUPPORT @		of INVESTMENT		
CORPORATE OVERHEAD:				
SALES & ADMINISTRATION		of INVESTMENT		
RESEARCH & DEVELOPMNT		of INVESTMENT		
SUBTOTAL CORPORATE OVERHEAD..				
INSURANCE & LOCAL TAXES:				
	2.0%	of INVESTMENT		5,880
EXCISE TAX:	$ 0.0900	per annual Gal of Capacity		5,040
ROYALTIES:	$ 0.0265	per annual Gal of Capacity		1,484
TOTAL FIXED COST (for cash flow calculations):			$	17,604 k per Year
				$0.31 per Gal
DEPRECIATION:				
		of INVESTMENT		

Note: Do not include Depreciation if total Fixed Cost is to be used in Cash Flow Calc.

TOTAL FIXED COST (for ROI calculations):	$	17,604 k per Year
		$0.31 per Gal

Cash Flow Analysis



CASH FLOW ANALYSIS

ALL FIGURES ARE IN $k

USER INPUT
INCOME
OPERATING COST
CAPITAL COST
SOLVED BY MACRO / USER

Sensitivity Analysis can be performed by pressing the Sensitivity Analysis button. A dialog box allows the user to select various options. For the Sensitivity Analysis Macro, X variables should be cells set by the user (yellow or blue). Y variables should be chosen to be calculated values or values solved by the worksheet (aqua or blue). Selling Price can be an X variable or a Y variable.
The Set Selling Price macro will break down if an unfeasible target value is entered.

COST OF CAPITAL = 4.5%
TOTAL CAPITAL COST = $294,000 k
SELLING PRICE = $1.56 per Unit
SALVAGE PERCENT= 0%
SALVAGE VALUE= 0

INFLATION = 1.9% ANNUALLY (Applies to all costs)
INFLATION = 1.9% ANNUALLY(Applies to selling price of product)
INCOME IS +, EXPENSES ARE -

Macros created by Jeremiah Zartman.
Modified 6/15/04

Total Replacement Cost Factor	0.0125	%
First year Replacement factor	0.03	%

	DESIGN		CONSTRUCTION 2010	STARTUP 2011	1 2012	2 2013	3 2014	4 2015	5 2016	6 2017	7 2018	8 2019	9 2020	10 2021	11 2022	12 2023	13 2024	14 2025
% OF CAPACITY			0%	50%	75%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
INCOME				43625	66681	90598	92319	94073	95860	97682	99538	101429	103356	105320	107321	109360	111438	113555
SALVAGE VALUE																		0
VARIABLE COST				2021	3089	4196	4276	4357	4440	4524	4610	4698	4787	4878	4971	5065	5162	5260
FIXED COST				-17604	-17938	-18279	-18627	-18981	-19341	-19709	-20083	-20465	-20854	-21250	-21653	-22065	-22484	-22911
DEPRECIATION				-58800	-95844	-59417	-38881	-38998	-18910	-4093	-3905	-3980	-4055	-4132	-4211	-4291	-4372	-17244
CAPITAL COST	0	0	-294000	-8820	-3675	-3745	-3816	-3888	-3962	-4038	-4114	-4193	-4272	-4353	-4436	-4520	-4606	-4694
LAND																		
WORKING CAPITAL			-31582															41885
ACTS RECEIVABLE	45			-5895	-3116	-3232	-233	-237	-242	-246	-251	-256	-260	-265	-270	-276	-281	-286
STARTUP COST			-8820	-35280														
GROSS INCOME			-8820	-66038	-44013	17097	39088	40452	62050	78404	80160	81683	83235	84816	86428	88070	89743	78659
INCOME TAX	38.9%		3431	25689	17121	-6651	-15205	-15736	-24137	-30499	-31182	-31775	-32378	-32993	-33620	-34259	-34910	-30599
DEPRECIATION				58800	95844	59417	38881	38998	18910	4093	3905	3980	4055	4132	4211	4291	4372	17244
NET CASH FLOW	0	0	-330971	3735	62162	62887	58715	59589	52618	47714	48518	49440	50379	51336	52311	53305	54318	102210

NPV = $203,022 k (Cash flows at end of each period)
NPV = $212,158 k (Cash flows at beginning of each period)

GUESS = 12.5% NPV = 0 SET BY MACRO ($0.00)
AFTER - TAX REAL IRR = 12.5%
TARGET= 12.5%

DEPRECIATION RATES (HALF-YEAR CONVENTION)

YEAR1	20%
YEAR2	32%
YEAR3	19%
YEAR4	12%
YEAR5	12%
YEAR6	5%

ROI CALCULATION

Third year income	90,598	$k/yr
Third year variable cost	4,196	
Third year fixed cost	-18,279	
Gross income	76,515	
Income Tax	-29,764	
Net Income	46,750	
Capital Investment (incl. Working Cap.)	353,975	$k/yr

ROI = 13.2%

PAYBACK PERIOD = 7.6 Years

Cash Chart


Cash Flow
Years
Cash Flow ($k)
$150,000
$100,000
$50,000
$0
-$50,000
-$100,000
-$150,000
-$200,000
-$250,000
-$300,000
-$350,000
-$400,000
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025