

Synthesis of Syngas and Production of Methanol from Waste Biomass

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Executive Summary

This project presents the design considerations and economic feasibility of a plant to produce methanol from waste biomass. It aims to investigate the feasibility of a new method of using concentrated sunlight from a heliostat field in order to reach the high temperatures required for biomass gasification. This technology is desirable because it repurposes waste biomass that would normally be disposed of into methanol which serves as a building block for hundreds of everyday products and as a clean energy source for transportation and homes. The feed product for the process is primarily biomass, composed of mostly cellulose and lignin, with smaller amounts of ash, nitrogen, chlorine and sulfur, solid zinc oxide and copper-zinc oxide catalyst pellets. Products from this process include primarily pure methanol along with small amounts of carbon monoxide and water. The problem statement specifies a final methanol yield of 56 million gallons per year with the product stream containing 99.97% methanol. The process consists of five main subprocesses: a solar thermal reactor, spray quench, zinc oxide reactor, raw methanol reactor and a downstream methanol purification column. Along with these main processes, the plant will include several other separators, heat exchangers, pumps, compressors and a heliostat field to provide energy from the sun. The solar thermal reactor is 25 meters in length with 3 silicon carbide reaction tubes of 0.06 and 0.07 meter inner and outer diameters respectively and is to be constructed out of stainless steel alloy. The solar thermal reactor with these design specifications achieved a 97% conversion of carbon from lignin and cellulose. The zinc oxide reactor is 1.81 meters in length, 3.34 meters wide, with 0.02 meter thick walls and a volume of 4,200 liters. The zinc oxide reactor achieves a 99.99% conversion of hydrogen sulfide and is to be constructed from stainless steel alloy. The methanol reactor is designed to be 1.74 meters long and 33,610 liters with 38,216 reaction tubes filled with 8724.64 kilograms of copper-zinc oxide catalyst pellets. The reaction tubes have 0.0254 and 0.0314 meter inner and outer diameters respectively. The methanol reactor produces 5,785 kilomoles per hour of raw methanol and is to be constructed from stainless steel alloy. The heliostat field is designed with two 180 meter tall towers and a total area of 453,924 cubic meters. The design includes six heat exchangers, all constructed of 316L stainless steel, five with shell diameters of 25 inches and a length of 16 feet and one with a shell diameter of 15.25 inches and a length of 10 feet. The spray quench has a volume of 42,500 liters and is to be constructed of 316L stainless steel. Four separators are included in the overall design - two cyclones, a distillation column, and a flash drum. The distillation column was found to have a diameter of 7 meters and a height of 38.1 meters. Three Fristam pump systems are included in the plant design. The first has 10 FPR 1161 pumps in series followed by a system with 10 FP/FPX 1151 pumps in series and finally a system of 2 FPR 751 pumps in series. Two Turbonetics compressors with 1000 Hp duties and 76% efficiency are also included in the design. In total, the plant demands \$1.092 billion in total depreciable capital, \$27.288 million in working capital, \$102 million per year in variable costs and \$30.2 million per year in fixed costs. At base case 12.5% IRR the plant's ROI is 11.8%. This plant design does not see positive cashflow for the two years of construction and the first nine years of operation. At the end of the plant's lifetime, cumulative cash flow totals \$1.052 billion, making this design an economical success. Based on environmental considerations including the amount of carbon dioxide emissions that can be avoided by implementing this design, it is recommended that this plant be built as designed. While not economically feasible for the first 11 years of the plant's life, the payoff over the course of 25 years is well worth the investment.

1 Project Description, Scope, and Background

Conversion of biomass into valuable or useful chemical compounds (such as syngas) has gained increasing prominence as greener processes in chemical manufacturing are becoming increasingly sought after. Biomass gasification can be both an effective method of producing synthesis gas and an effective disposal method for waste biomass from agricultural processing. The synthesis gas can then be used in the production of organic compounds such as fuels or, as modeled by this project, methanol. One of the primary downsides of this method of synthesis gas production is the high temperature required to obtain high conversion of biomass into carbon monoxide rather than carbon dioxide. The following model of the methanol production plant and required equipment aims to investigate the feasibility of one solution to the challenge of obtaining the required high temperatures: the use of concentrated sunlight in order to heat the biomass reactor to the necessary temperature. A secondary method also being tested is the use of methane as a sweep gas and supplier of hydrogen gas to help increase the selectivity of biomass reaction to carbon monoxide rather than carbon dioxide (as discussed above).

Previous research in this area has largely focused on gasification of biomass to syngas in “fixed bed, in fluidized bed, or in entrained flow reactors” (Demirbas, 2007), which can then be converted to hydrocarbons (including methanol) in a process known as the Fischer-Tropsch synthesis process^[1]. This process has been heavily investigated, and both the hydrocarbons that can easily be obtained and the catalysts required are well-established. However, these studies focus on the production of both carbon monoxide and dioxide in biomass gasification, as the gasification reaction is typically performed at a low enough temperature that selectivity of carbon monoxide is not as good. As mentioned previously, this model aims to improve selectivity through sweep gas and a high temperature reactor. Solar thermal reactors, powered by heliostat fields concentrating sunlight, have also been studied in small scale theoretical models but have not been implemented as much in industry and large scale manufacturing and processing. As such, this investigation attempts to combine the previous research into Fischer-Tropsch synthesis reactions from syngas with a new and revolutionary system of reactors to better optimize green syngas production from waste biomass.

In addition to considering the technical viability of methanol production from biofuel and methane, the economic feasibility and profitability of the methanol production process will also be considered. The cost of all required reactors and supporting equipment such as heat exchangers and pumps will be taken into account, as well as basic operating cost analysis taking into account land purchase and development, raw materials, utilities, waste management, inflation and a carbon credit (among other costs). For this process, biomass is the primary raw material entering the system. The biomass is composed primarily of cellulose and lignin, as well as smaller amounts of ash, monatomic nitrogen and chlorine, and sulfur. The secondary reactants fed into the system are methane and water. Additionally, solid zinc oxide is required (in relatively small quantities) for the solid zinc oxide reactor in order to remove waste products of

hydrogen sulfide and hydrogen chloride from the process stream. Finally, a solid catalyst is required to fill the tubes and promote the formation of the primary methanol product in the raw methanol reactor. Non-reactive utility streams will also be needed in order to provide heat exchange essential to the heating and cooling of the process streams to the desired temperatures (with the exception of the heating of the solar thermal reactor, which is accomplished primarily with concentrated sunlight from a heliostat field.)

An overall summary of the reactors and key components for this production process is given as follows. Waste biomass is fed, along with water and methane, into the solar thermal reactor. The solar thermal reactor is heated to a high enough temperature to favor the carbon monoxide rather than carbon dioxide reaction of biomass using concentrated sunlight from a nearby heliostat field. The reaction is quenched and a water-gas shift reaction occurs to obtain a process stream with near the desired syngas ratio of 2 moles of hydrogen gas per mole of carbon monoxide gas. A wastewater stream from the spray quench system removes the majority of the water fed into the spray quench from the process stream. A cyclone removes any remaining particular solid waste from the process stream. Purification of the syngas is performed in the zinc oxide bed, which removes hydrogen sulfide and hydrogen chloride gas by reacting them with zinc oxide, producing solid zinc sulfide and zinc chloride waste byproducts which are then removed. With the syngas stream purified, the process stream is fed into a catalytic methanol reactor and flash separation is performed to extract the methanol as much as possible from the other components. A recycle stream around the methanol reactor accounts for the low conversion obtained on each pass. An overall recycle stream for the reaction system is also implemented, though a fraction of the vapor stream from the flash separation is purged entirely. It is worth noting that the majority of these processes aim to produce and purify the syngas stream to the desired composition and purity, and the production of the actual methanol product occurs exclusively in the raw methanol reactor and flash separation step.

2 Environmental, Health, and Safety

2.1 Site Location

It was recommended that the downstream processing site also be located in Southern California. A general recommendation for choosing site locations for high volume products is to locate them close to the target market. California's biofuel market is the second largest in the country. Additionally, we wanted to take into consideration the location of the heliostat field which would likely be in the Mojave/Death Valley region of Southern California. With this in mind, the nearby Pacific Ocean should be taken advantage of since international distribution of this product was a possibility. While real estate is expensive in the Los Angeles area, the labor prospects that this location would attract would balance out the real estate/tax costs since Los Angeles is an attractive destination for professionals. Lastly, distribution of waste needed to be considered which would involve consideration of appropriate landfill disposal sites. These sites are discussed in section 2.3 and results of the section were used ahead of time to determine the

ultimate location of the plant. The exact location of the plant was chosen to be Long Beach, California. Some other general factors considered included the availability of transportation facilities, steady year-round temperature at the heliostat location, and the availability of key utilities such as cooling water, possibly sourced from the ocean.

2.2 Occupational Health and Safety Regulations

The primary document that had to be adhered to for both the methanol production plant and the downstream processing was Title 8 of the California Code of Regulations^[2.2.1] alongside the California Labor Code^[2.2.2]. Under the California Occupational Safety and Health Act, all employers are legally obligated to “provide a safe and healthful workplace for their employees.” California’s OSHA requirements are aligned with Federal OSHA requirements. Some key pieces of regulation were cited in the following sections.

2.2.1 Hazard Classification

Manufacturers, importers, and distributors are required to evaluate if chemicals produced in the workplace are hazardous, and classify them accordingly. Proposition 65^[2.2.1.1] deals specifically with chemicals that cause cancer, birth defects, or reproductive harm. Manufacturers must obtain Safety Data Sheets-- updated within the last three months, and in English-- for every chemical that they produce. Employers must ensure that containers of hazardous chemicals are labeled, tagged and marked. They must also ensure that employees are properly trained whenever a new hazard is introduced to the workplace, or within 30 days of the employer receiving revised SDS information.

2.2.2 Inspections

Advance notice of inspections to employers is a violation of Labor Code Section 6321 - with some exemptions. Violations are classified as regulatory, general, and serious, with separate provisions for willful and repeat violations.

2.2.3 Process Safety Management

All employers must follow the guidelines laid out in the Recognized and Generally Accepted Good Engineering Practices for Process Safety Management (RAGAGEP) by the Rand Corporation^[2.2.3.1]. RAGAGEP recognizes that the greatest expertise in defining a safe system lies with the industry-specific communities. Therefore they must come together to: 1. develop a list of organizations that qualify as sources of RAGAGEP, 2. identify a common standard for documents and data that are to be used for the RAGAGEP, 3. make the language enforceable, (ie. recommendations should not include words such as “should,”), and 4. create clear guidelines on how to evaluate internal standards. It is encouraged that the managers of this plant participate in their local industry communities.

2.2.4 Pressure Vessel-specific Regulations

According to Section 460, Article 2 of Title 8, all pressure vessels that exceed 15 psig must be designed in accordance with the American Society of Mechanical Engineers code. The maximum allowable pressure is calculated in accordance with the ASME Code, with a factor of safety not less than 4. Section 560 gives a list of safe practices that pertain to the operation, transfers and transportation, and requirements for relief devices.

2.3 Waste Stream Management

The primary waste streams from this process were out of the cyclone solids separator and the solid zinc oxide bed. The first waste stream consisted entirely of solid ash, and so an appropriate location had to be determined to dispose of this waste. Covanta^[2.3.1] is a company in the Long Beach region of Los Angeles that can dispose of biomass waste such as wood ash in large quantities. Utilizing their services would be the most feasible way to dispose of the waste stream out of the cyclone separator. The solid zinc chloride could be disposed of in any landfill, though consideration should be made as to whether a target market could be found willing to purchase this byproduct instead of disposing of it. There were also several aqueous waste streams. It was assumed that these would be sent to wastewater treatment facilities, either locally or on-site, for remediation.

2.4 HAZOP

A Hazard and Operability Study is used to identify scenario based hazards that may affect the productivity of a plant, and/or jeopardize the health and safety of the workers and the surrounding community. HAZOPs can be conducted for multiple parameters of each unit of the overall process. An example is given here for one unit of each of the two production plants: the solar thermal reactor of the upstream process and the distillation column of the downstream methanol purification plant.

Table 2.4.1. HAZOP: Solar Thermal Reactor

Deviation	Possible Causes	Consequences	Safeguards	Recommendations
More Flow	1. Too Much Recycle	Lack of product production. Accumulation which can overfill unit	Potential recycle stream and separator added to appropriate streams	NNR*
Less Flow	1. Not Enough Recycle	Products too hot, loss of energy	Potential scale-down of energy provided to reactor based on feed rate (implementation of flow meter	NNR*

No Flow	1. Blocked Equipment(FEED MIX and Pump)	Wasted energy	Reactor shutdown through flow meter	NNR*
More Pressure	1. Too much recycle	Reactor fails to reach conversion	Potential recycle stream and separator added to appropriate streams	NNR*
More Pressure	2. Buildup of Material in Reactor	Reactor could seize and malfunction, financially devastating	Reactor Shutdown	NNR*
Low Pressure	1. Not enough recycle flow	Reactant products could be too hot	Lower Temperature control	NNR*
Low Pressure	2. Blocked mixer (feed mix)	Wasted energy, buildup in piping	Shutdown, redirection of stream through additional piping	NNR*
High Temperature	1. Too much energy provided by Heliostat	Wasted Energy, bad selectivity	On-site capacitors to store energy, required redirection circuit	NNR*
High Temperature	2. Inadequate Cooling - Runaway Reaction	Explosive/hazardous conditions experienced by plant, broken reactor and	Reactor Shutdown, Secondary cooling source	NNR*
Low Temperature	1. Not enough energy provided by heliostat	Inadequate conversion, wasted reagents and energy	Installation of backup energy source (temporary), slower reactant feed	NNR*
Low Temperature	2. Deteriorated Piping Material -Lack of Radiation	Inadequate conversion, wasted reagents and energy	Reactor Shutdown, piping replacement	NNR*
Wrong Composition	1. Broken Water Pump (PUMP-1)	Imbalance of reactions, production of undesired product	Redirection of 2nd water pump with increase in supply (pump has to have high	NNR*

			capacity)	
Wrong Composition	2. Too much recycle	Imbalance of reactions, production of undesired product	Flow meters on recycle pipeline before first mixer, redirection of material into storage tank	NNR*

**no new recommendations are required as the process is being designed*

Table 2.4.2 HAZOP: Distillation Column

Deviation	Possible Causes	Consequences	Safeguards	Recommendations
More Flow (Vapor)	1. High Reboiler Heat Duty	Impure methanol product	Cooling Fluid	NNR*
More Flow (Liquid)	2. Too much condenser utility	Low rate of methanol product	Temperature transmitters with alarm to alert operators to adjust controls	NNR*
Less Flow (Liquid)	3. Inadequate Condenser utility	Impure methanol product	High temperature alarm, add another heat exchanger if necessary	NNR*
Less Flow (Liquid)	4. Low reboiler heat duty	Low rate of methanol product	Low temperature alarm, add another heat exchanger if necessary	NNR*
No Flow	5. Broken pump (PUMP-3)	Wasted energy, damaged equipment	Arrange for periodic maintenance	NNR*
More Pressure	6. Too much feed	Inefficient separations, impure product	Continuous monitoring on the part of operators, regulate via control valve	NNR*
More Pressure	7. Too much recycle	Inefficient separations, impure product	Flow indicator, operators should be trained to regulate via control valve	NNR*

Low Pressure	8. Reflux ratio too high	Too much product	Flow indicator should alert operators, column pressure and temperature should be adjusted immediately	NNR*
Low Pressure	9. Broken pump	Not enough product	Arrange for periodic maintenance	NNR*
High Temperature	10. Heat duty too high	Impure product	Regulate the flow of process fluid into the reboiler.	NNR*
High Temperature	11. Broken pump	Not enough product	Arrange for periodic maintenance	NNR*
Low Temperature	12. Heat duty of the reboiler set too low	Not enough product	Regulate the flow of process fluids. Add another heat exchanger if necessary.	NNR*
Low Temperature	13. Feed enters at a lower temperature	Not enough product	Monitor upstream process for deviations from standard operating procedures.	NNR*
Wrong Composition	14. Column is purged incorrectly	Impure product, flammable conditions	Nitrogen pressure must be regulated through a control valve	NNR*
Wrong Composition	15. Impurities from upstream process	Impure product	Install a composition analyzer	NNR*

**no new recommendations are required as the process is being designed*

2.5 Layer of Protection Analysis

A Layer of Protection Analysis, or LOPA, is conducted for a specific hazard scenario in order to assess the likelihood and the availability of sufficient layers of protection^[2.5.1]. This is a semi-quantitative method that can be further supplemented by other quantitative methods. A

LOPA is usually conducted first, and if the results from it are unsatisfactory, a Qualitative Risk Analysis might be warranted. The major steps of a LOPA are described below:

1. Identify a consequence that is to be investigated. This could be, “Conditions in the solar thermal reactor could become explosive and hazardous.”
2. Identify an accident scenario that could lead to the consequence. High temperatures could cause the scenario described above.
3. Next, the initiating event is defined, and its frequency estimated. In the case of the solar thermal reactor, it could be because of inadequate cooling of the reactor.
4. The protection layers for the hazard are defined, and the probability of each of the layers failing are estimated.
5. The frequency of the initiating event, as well as the frequency of the protective layer failing are both combined to evaluate the overall risk.
6. The risk and the consequences of the accident scenario are evaluated to determine if they are acceptable or not. Different organizations will have different standards for what they deem is acceptable risk.
7. If the risk level is unacceptable, then additional protective layers are required.

Examples of protective layers and their governing hierarchy are given in Figure 2.5.1, by Crowl & Louvar ^[2.5.1].

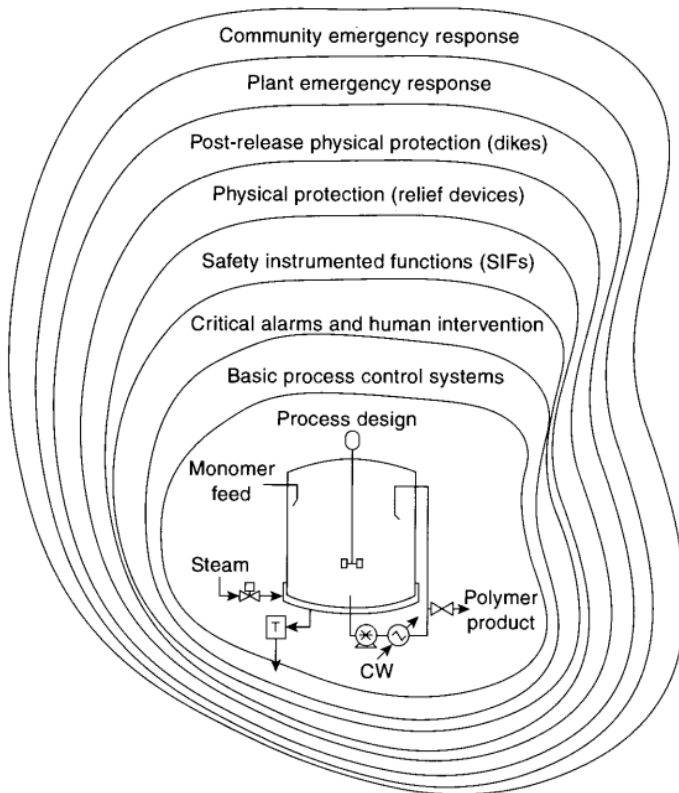


Figure 2.5.1 An Example of protective layers for a CSTR

These inherently safer designs, containment measures, and emergency responses are described below in section 2.5.1.

2.5.1 Process Design

Process designs should aim for inherent safety, i.e, minimizing the reliance on control systems and emergency operating procedures. The four key guidelines outlined by Crowl and Louvar can be followed: minimize, substitute, moderate, and simplify. Examples of how these guidelines can be applied in designing this methanol production plant are:

- To minimize the quantity of hazardous raw materials that are located in our inventory, or final products in store, good process control should be implemented. Large quantities of our final product, methanol, accumulating, could pose a flammability risk.
- Substitution involves replacing a dangerous condition for one that is less of a risk. As detailed in Section 5.3, the process utilities for the heat exchanger have been chosen to be water, as opposed to other heat transfer fluids such as hot oil.
- Moderation requires minimizing the severity of effects. Since this process deals with several flammable components, it is necessary to barricade control rooms to ensure they remain operable even in the event of emergencies.
- The last guiding principle is simplification. It is important to ensure ease of operation. Piping systems must be easy to follow. Emergency procedures must be depicted someplace visible. Control panels must be easy to read, and all relevant plant personnel must be trained periodically to refresh their knowledge.

2.5.2 Control Systems

Control systems are the first line of defense (shown in Figure 2.5.1) and are used to not only keep a unit from entering dangerous regions of a given variable but also to keep the unit operational so that desired product is obtained. These controls are most notable and common for equipment that have more hazards than smaller equipment such as a pump or heat exchanger. The following table shows control systems for major equipment in this methanol process.

Table 2.5.2.1 Process controls list of notable equipment

Equipment	Temperature Control?	Pressure Control?	Flow Control?
Solar Reactor	Yes	Yes	No
WGS Reactor	Yes	Yes	No
Spray Quench HX	Yes	No	Yes
Cyclone	No	Yes	Yes
Gas-Cleaning Bed Reactor	Yes	Yes	No

ZnCl ₂ Separator	No	Yes	Yes
Compressor	No	Yes	No
MeOH Reactor	Yes	Yes	No
MeOH Separator	No	Yes	Yes
Distillation Column	Yes	Yes	Yes

2.5.3 Alarms

In the case that the controls fail and a variable exceeds its expected/allowed range, a next line of defense needs to be ready. Alarms are a simple way for processes to be manually modified without completing halting an operation. A noticeable trend of these lines of defense is that for every additional layer of protection that is called for there is about an equal decrease in production that follows. Alarms sound to both operators on the ground next to the equipment and often to the overhead staff supervising. This layer of protection signals to nearby operators to make manual changes to the equipment by switching a lever or closing a valve (e.g.). An alarm is used in the case that the process has entered a dangerous condition that will not irreversibly deter a process but can be hazardous if left untreated. Below are some alarms expected to be installed in notable equipment of this methanol processing plant.

Table 2.5.3.1 Alarm systems of notable equipment

Equipment	Temperature Alarm?	Pressure Alarm?	Flow Alarm?
Solar Reactor	Yes	Yes	Yes
WGS Reactor	Yes	Yes	Yes
Spray Quench HX	Yes	No	Yes
Cyclone	No	Yes	Yes
Gas-Cleaning Bed Reactor	Yes	Yes	Yes
ZnCl ₂ Separator	Yes	Yes	Yes
Compressor	No	Yes	Yes
MeOH Reactor	Yes	Yes	Yes
MeOH Separator	Yes	Yes	Yes
Distillation Column	Yes	Yes	Yes

2.5.4 Safety Instrumented Functions

Processes are designed such that if an alarm is not attended to by an operating and action with appropriate quickness, that an automated response initiates. These responses are referred to as safety instrumented functions (SIF). These functions will severely alter the condition of an equipment such that the product of that process will be affected, possibly to the point where it is out of range of specification. These responses are usually programmed to initiate at a point at which the excess condition has run for an amount of time to which danger is apparent. Below are some expected SIF's that will be installed to this methanol processing plant. Note that there are more SIFs for each piece of equipment and that only the most important ones are listed.

Table 2.5.4.1 Important SIF's of notable equipment

Equipment	Condition Exceeded	Resulting Action
Solar Reactor	Temperature	Energy sources is diminished, heat transfer fluid (of colder temperature) is flown through reactor
WGS Reactor	Temperature	Heat transfer fluid (of colder temperature) is flown through reactor
Spray Quench HX	Flow Rate	Exit hatch is opened in shell such that flow is disposed of
Cyclone	Flow Rate	Exit hatch is opened in cyclone so that flow is unclogged
Gas-Cleaning Bed Reactor	Temperature	Heat transfer fluid (of colder temperature) is flown through reactor
ZnCl ₂ Separator	Temperature	Heat transfer fluid (of colder temperature) is flown through reactor
Compressor	Pressure	Pressure Relief
MeOH Reactor	Pressure	Pressure relief valve is opened
MeOH Separator	Temperature	Heat transfer fluid (of colder temperature) is flown through reactor
Distillation Column	Flow Rate	Weir is raised or lowered so that flow is adjusted, utility of condenser is increased or decreased, energy supply of reboiler is decreased

2.5.5 Relief

Relief devices are the next protective layer after safety instrumented functions and serve as a last line of protection in terms of preventing the hazard. These devices actually shut the operation down so that it no longer proceeds by halting any sort of mechanical and thermal action involved in that process. This measure is usually a last resort because it essentially spoils any material that was actively in the process as equipment has to be cleaned out afterwards such that the process is run from scratch. Such initiatives are taken when a process is in immediate danger due to the prior SIF being ineffective. Because a lot of processes get exponentially more hazardous with time, these initiatives are usually taken very shortly after SIFs are initiated so that things do not get out of control before it is too late. Listed below is a table containing expected relief measures for notable equipment in this methanol processing plant.

Table 2.5.5.1 Relief measure of notable equipment

Equipment	Relief Measure	Result
Solar Reactor	Cut off energy supply and material feed	Shutdown
WGS Reactor	Cut off energy supply and material feed	Shutdown
Spray Quench HX	Cut off material feeds	Shutdown
Cyclone	Cut off material feed	Shutdown
Gas-Cleaning Bed Reactor	Cut off energy supply and material feed	Shutdown
ZnCl ₂ Separator	Cut off material feeds	Shutdown
Compressor	Halt mechanical motion, cut off material feeds	Shutdown
MeOH Reactor	Cut off energy supply and material feed	Shutdown
MeOH Separator	Cut off energy supply and material feed	Shutdown
Distillation Column	Cut off energy supply to reboiler and material feed	Shutdown

2.5.6 Personal Protective Gear

In the case that the shutdown (relief) methods were ineffective in alleviating the apparent hazards, responses must be taken to protect those nearby the process, often described as anybody on the grounds of the process plant. Most personal protective equipment (PPE) is regulated to be worn at all times because in the cases that shutdown measures are ineffective, catastrophic conditions occur in the manner of seconds, leaving little to no time for nearby workers to respond by dressing up and equipping themselves with further equipment. This layer of

protection is designed to keep workers from being exposed to hazardous conditions while in the presence of them. Unfortunately, most process incidents are on the magnitude that PPE is simply ineffective if someone is in a certain range of an exploding reactor for example. This equipment is more so of a protection against minor incidents (gas leakage) in close proximity or large incidents from a greater proximity. Listed below is a table containing basic equipment that would prove beneficial to anyone on-site.

Table 2.5.6.1 Required personal protective equipment

Equipment	Hazards Addressed
Hard Hat	Falling objects, falls.
Gas Mask	Toxic vapors
Glasses	Projectile metal shards, heat sources (steam)
Ear muffs	Excessive noise from equipment
Gloves	Hot temperatures and sharp objects
ARC Gear	Fire and spills of chemicals
Boots	Sharp and/or falling objects

2.5.7 Plant and Community Response

The plant and community response is more of a second iteration of the personal protective equipment. The first priority is to protect the people closest to the incident since they are the most vulnerable to repercussions and safety defects. From there, it is the responsibility of the plant to inform the nearby community of an immediate threat that would warrant evacuation. This communication is most often relayed through the local police department since they have expertise in these procedures. The most common reason for evacuations are large-scale gas leakages. It is in the best interest of the community that a more than expected radius of gas spread is foreseen such that more homes/buildings are evacuated than necessary. Most plants are expected to have pre-calculated radiuses of evacuation for different accident scenarios.

2.6 Quantitative Risk Analysis

Table 2.6.1 HAZOP Ranking

Risk	Likelihood	Severity	Ranking
Burst Pipe	1	3	B
Leaking Pipe	1	4	A

Blocked Equipment	2	4	A
Runaway Reaction	3	1	C
Broken Pump	2	4	A
Mild Earthquake	3	2	B
Severe Earthquake	4	1	B
Tidal Wave	4	1	B
Meteor Impact	4	1	B

2.7 MSDS Summary

Table 2.7.1. MSDS Summary

Species [Source]	Chemical	Flash Point(C)	Flammability	Health	Reactivity	Special Considerations
Methanol [2.7.2]	Alcohol	12	3	1 Eye: Moderate Skin: Moderate Ingestion: Fatal Inhalation: Toxic	0	Extremely flammable
Methane [2.7.10]	Hydrocarbon	-104	4	2 Eye: Burns Skin: Minimal Ingestion: Fatal Inhalation: Toxic	0	Extremely flammable
Zinc Oxide [2.7.15]	Amphoteric Oxide	N/A	0	2 Eye: Moderate Skin: Moderate Ingestion: Fatal Inhalation: Toxic	0	N/A
Lignin [2.7.13]	Hydrocarbon	N/A	1	1 Eye: Moderate Skin: Moderate Ingestion: Fatal Inhalation: Moderate	0	N/A
Cellulose [2.7.1]	Polysaccharide	N/A	1	1 Eye: Minimal Skin: Minimal Ingestion: Moderate Inhalation: Moderate	1	N/A
CO [2.7.5]	Oxocarbon	N/A	1	Eye: Minimal Skin: Minimal Ingestion: N/A Inhalation: Fatal	2	Very Toxic for inhalation

CO2 [2.7.4]	Oxocarbon	N/A	0	3 Eye:Minimal Skin:Minimal Ingestion:N/A Inhalation: Toxic	0	non-combustible
H2 [2.7.7]	Diatomic Gas	N/A	4	0 Eye:Minimal Skin:Minimal Ingestion:N/A Inhalation: Toxic	0	Extremely flammable
Sulfur [2.7.3]	Non-metal	207	1	1 Eye:Burns Skin:Burns Ingestion:Moderate Inhalation: Moderate	0	Combustible product is sulfur dioxide
Chlorine [2.7.6]	Halogen Gas	N/A	0	4 Eye:Burns Skin:Burns Ingestion:Fatal Inhalation: Fatal	0	Very hazardous upon any for of exposure
Hydrogen Sulfide [2.7.9]	Non-metal sulfide	N/A	4	4 Eye:Minimal Skin:Minimal Ingestion:N/A Inhalation: Fatal	0	Extremely toxic gas, fatal is small dosages
Hydrogen Chloride [2.7.8]	Strong Acid	N/A	0	3 Eye:Burns Skin:Burns Ingestion:N/A Inhalation: Fatal	1	Dangerous to skin
Zinc Oxide [2.7.14]	Amphoteric Oxide	N/A	0	2 Eye:Moderate Skin:Moderate Ingestion:Moderate Inhalation: Toxic	0	Not a very hazardous chemical
Zinc Sulfide [2.7.12]	Inorganic Compound	N/A	0	2 Eye:Burns Skin:Moderate Ingestion:Moderate Inhalation: Moderate	0	N/A
Zinc Chloride [2.7.11]	Inorganic Compound	N/A	0	3 Eye:Burns Skin:Burns Ingestion:Toxic Inhalation: Moderate	0	N/A
Nitrogen [2.7.16]	Non-metal diatomic gas	N/A	0	0 Eye:Moderate Skin:Minimal Ingestion:N/A Inhalation: Minimal	0	Inert Gas

2.8 Other Miscellaneous Best Operating Practices

2.8.1 Permits

Permits must be obtained for non routine activities in order to prevent accidents.^[2.5.1] Operating personnel must be informed of the risks involved and supplied with a detailed overview of the tasks permitted while the work is being performed, as well as how to transition back to the normal operating mode. Some relevant permits for both the methanol production plant and the downstream processing plant are given below.

Lock-Tag-Try Permit:

This permit prevents damage that could occur due to the accidental release of stored energy from equipment. The procedure is as follows: 1. De-energize the system, 2. Lock the equipment to prevent activation, 3. Tag the equipment to warn against re-energizing the equipment, 4. Attempt to re-energize the equipment to ensure the locking process works, 5. Conduct the necessary maintenance, 6. The supervisor is then responsible for removing the lock after she has ascertained that it is safe to return to normal operation.

For the raw methanol production plant, it is of highest importance that this procedure is followed when employees are conducting maintenance on equipment with moving parts, especially FEED-MIX, SQ-MIX, and MIX-2. When de-energizing these pieces of equipment, electrical connections must be unplugged, relief devices released, and pressurized steam lines such as the one in the SQ-SPLIT released as well.

Hot Work Permit:

This permit is valid for one shift and is necessary when any hot works are being conducted. This includes welding, soldering, torch cutting, etc. These works result in an ignition source that is a hazard in the presence of flammable liquids and gasses. There are many flammable chemicals listed in the MSDS table (Table 2.7.1) that need to be considered when performing hot work. Welding around flammable materials has resulted in countless process incidents over the years.

2.8.2 Safety Reviews and Accident Investigations

Periodic safety reviews are required to appraise all personnel working in the plant of the associated risks, and to prevent the recurrence of accidents. General features of safety reviews include: developing detailed process descriptions with the help of PFDs and P&IDs to illustrate the different equipment, and the associated mass and energy flows; list of chemicals and their hazard information; standard operating procedures such as start up, shut down, as well as those requiring permits as detailed in the previous section; sharing all findings of accidents investigations in related plants within the plant, and to others in the field; and developing recommendations to improve the overall design in order to minimize or eliminate known hazards.

2.8.3 Runaway Reaction Prevention

Any reaction that is exothermic has the potential to create a runaway reaction scenario. This is where energy generated by a process is used subsequently to create more energy, thus increasing the total amount of energy in equipment exponentially with time to the point where it is uncontrollable. Runaway reactions are the biggest threat to any process plant because they are relatively nuclear and often release a magnitude of energy that feasibly overcomes nearby equipment. Runaway reactions are given a lot of attention by the layers of protections mentioned previously as the responses of equipment are very time-sensitive. The reactions being performed are done so in reactors that occupy volumes up to a few cubic meters which means there is plenty of potential for these equipment to cause damage to the surrounding of the processing plant.

3 Approach and Premises

3.1 Overview of Approach

Following the initial hand-calculated material and energy balances, various softwares were used for the majority of the rest of the major designs. Aspen Plus was used in order to gain a better understanding of the chemical compositions, temperatures, and pressures of the various components and streams that composed the reactor system. Aspen Plus also allowed us to take into account the effects of the true conversion of the water-gas shift reaction and the two recycle streams present in the system, updating both the material and energy balances to more system-accurate values. In Aspen Plus, the entire process for the production of the raw methanol was modeled. This included the zinc oxide and raw methanol reactors, heat exchangers and pumps, and components to emulate the behavior of the solar thermal reactor. Secondary modeling was performed in Aspen HYSYS to model the distillation column used in the purification of the raw methanol to the final product.

The majority of the component designs were performed using hand calculations in Microsoft Excel for ease of organization and calculation. These calculations used values provided by Aspen as a basis for the flow rates, compositions, temperatures, and pressures, and applied heuristics and methods described earlier in the course in order to obtain a design for the non-reactor parts of the system. The heliostat field design was done based on the Excel heliostat design files provided by Mr. Lewandowski. The reactors could not be designed directly using hand calculations, as each reactor required several related differential equations to describe the behavior of the reactions occurring in each reactor. Chemical species material balances, pressure drops, and energy balances had to be solved simultaneously along the length of the reactor to obtain a clear picture of the behavior of the reactor and the reactions within it. MatLab was used to solve these differential equations simultaneously, using ode45 specifically.

Following the design of the various components, additional analysis of the system was performed. Heat integration was done in Aspen Energy Analyzer, based upon the updated Aspen Plus file that included all of the heat exchangers involved in the reaction process. Profitability

and economic analysis was also performed, using the Excel economics tool provided by Professor Weimer. These tools provided additional analysis of the chemical processing plant as a whole, rather than only looking at the process component by component.

3.2 Project Management

A key element in determining how tasks were to be divided up and in establishing a timeline for the project was the understanding the chronological order that tasks needed to occur in. Many of the areas of this report required the completion of other steps in the process, and time had to be allocated such that there would be sufficient time to work on the later tasks prior to the deadline. Initial approximations about when tasks could be completed and the duration of time that was reasonable to dedicate to each were made prior to beginning the project. Accordingly, some deviations from the expected timeline did occur. It was not necessary to adjust the Gantt chart to match these deviations, as it instead provided a summary of what needed to be accomplished and primarily served as a guideline for deadlines of deliverables and the allocation of various parts of the project to the various group members.

The Gantt chart was created based upon expected availability and the established deadline, and served to designate tasks to each of the group's five members. Some of these tasks were completed individually while others, typically those that could be divided up into multiple subparts or that were expected to be more pivotal to future work were made a collaborative effort between multiple group members. Regardless of the amount of people assigned to a task, communication regarding the progress of each task—specifically, issues encountered or deviations from schedule—were expected in order to keep the group informed regarding the timeline of task completion. The chart itself, displayed below in Figure 3.2.1, acted as a visual summary of the tasks, timeframes, and division of labor for the team. A written summary of key information from the chart is provided below as well.

The initial material and energy balances, designed to give a general understanding of the feed material and energy requirements prior to the more formal Aspen model, were performed first. While the Gantt chart shows these tasks as being divided up with two members responsible for the material balance and only one for the energy balance, the two remaining group members also assisted heavily with the energy balance. These hand-calculated balances were considered a key step prior to beginning work on the Aspen Plus simulation, but also helped to formulate an understanding of the process as a whole and the reactions and chemical species that were involved in it. Accordingly, it was essential that the whole group should be involved in this first step of the process.

Similarly, the Aspen Plus portions of this project were divided up such that each group member participated on at least one section of the simulation. While this did mean that some group members gained an understanding primarily of a particular section, the collective involvement in

the Plus simulation encouraged at least a general understanding of the other sections of the production system and how they fit together. This overarching knowledge from each group member was deemed a necessity even as other tasks were divided up: while it was necessary that group members focus on different parts of the process in order for the project to be completed, an understanding of how the various different parts fit together was essential. The further processing of the methanol in the distillation column was considered to be outside of the main process, and so it was not considered necessary to encourage collective group involvement. The relative simplicity of the processing in the distillation column also made this division reasonable. The Aspen HYSYS file work was handled almost exclusively by an individual member who expressed the most confidence in Aspen related work.

Only once the process had been fully modeled in Aspen could work be performed in designing the various components present in the system on a more in-depth level. Three of the members were each assigned one of the three main reactors as their primary design responsibility. The reactors required an extensive amount of research into specific reaction rates and additional balances along the reactor length, such as pressure drop equations or energy balances. Having one group member who fully understood the work being done for their respective reactor, and who was responsible for all work done involving the research, coding, and reactor design process, was decided to be the best course of action. The process for designing a reactor was complex in that multiple different sources of information had to be drawn from and a thorough understanding of the reactor was required. Communicating information and code between group members if multiple people were assigned to work on the same reactor simultaneously would have been difficult and likely detracted from each individual's understanding of the system and ability to provide useful contributions. The remaining elements of the system that needed to be designed through hand calculations were divided among all the group members, with more hand-calculation design responsibilities given to the group members who were not responsible for a reactor.

While designing reactors and the other components of the system, group members were also tasked with written components in order to keep the group on schedule in terms of completing the project report. Writing code and performing hand calculations was only part of the responsibility of each group member, as they were also expected to provide the writing of the formal report for their designated components. Additional sections of the report which required no calculation were also divided up so that the group member's workloads were as even as possible. These written portions were to be completed during periods when the reactor and component designs could not be worked on due to holdups in the process or while waiting to meet with the group or the professors for assistance and guidance. Much of the written portion was expected to be completed during the one-week Thanksgiving break that fell during the timeframe of the project.

Finally, the group planned to come together to complete the report once all the calculation and design portions had been completed. Formatting and editing of the report was expected from all group members, though some tasks such as the references or nomenclature tables were headed by the team member designated on the Gantt chart. The Gantt chart also provided a timeline for completion two days before the due date, accounting for possible delays. Through this division of labor, we aimed to produce quality technical work and clearly communicate what had been accomplished within the timeframe allowed for this extensive project.

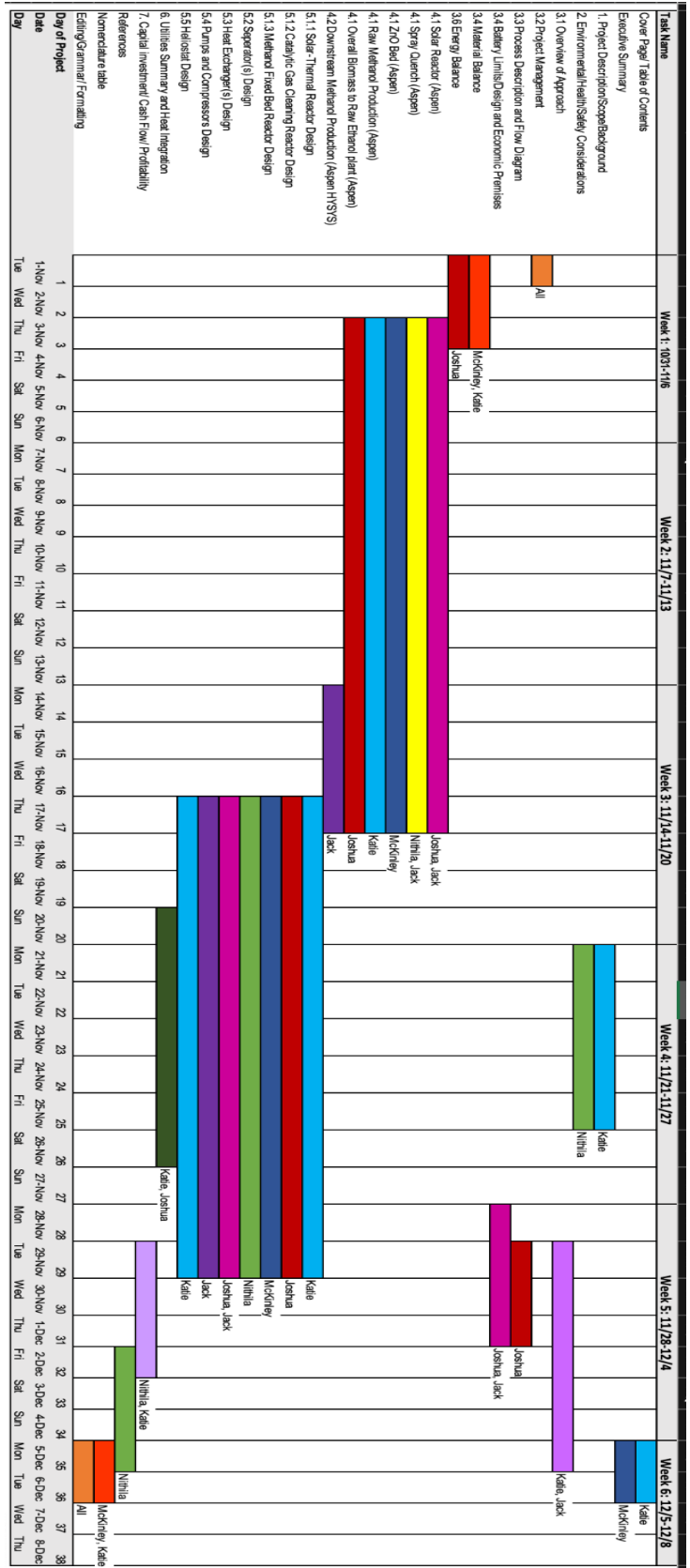


Figure 3.2.1 Gantt chart visually representing time frames and divisions of tasks

3.3 Process Description and Flow Diagram

Figure 3.3.1 showed the ideal process that will be used to produce methanol. The units were listed in green with labels. The flow streams, both energy supplied and actual material streams, were labeled in blue. The process began in the top left of the PFD, where biomass, methane, and the recycle stream were combined to a singular stream which was fed to a high-temperature, high-pressure solar reactor that was additionally fed a water stream powered through a pump (Pump-1). This reactor converted biomass into carbon monoxide, hydrogen chloride, hydrogen sulfide, and hydrogen gasses which were fed to an equilibrium reactor (WGS) to be converted into carbon dioxide and hydrogen. In actuality, both of these reactors occurred within the solar thermal reactor, but for the sake of modeling they had to be treated separately. There were two product streams shown leaving this reactor, the top one being the vapor product which contained everything except the solid ash which exited through the solid stream on the bottom of the reactor. These two streams were combined in a mixer (Mixer-2) and sent to the spray quench operation.

The spray quench operation used a heat exchanger (Spray Quench HX) to cool this stream with water pumped (Pump-2) through the other side of this heat exchanger. The resulting steam from this heat exchanger was sent to a splitter, with only a small amount of this steam remaining in the cooled process stream. This addition was performed in another mixer (Mixer-3) and the resulting stream was sent to the cyclone separator to dispose of the solid ash waste. The purified stream was then heated to a high temperature using a shell-and-tube heat exchanger for the zinc oxide bed reactor (Heat Exchanger-1). The resulting steam was fed to the reactor (Gas-Cleaning Reactor) along with a zinc oxide feed. This reactor removed hydrogen sulfide and hydrogen chloride by reacting them with zinc oxide. The reactor produced zinc sulfide and zinc chloride which were sent to a separator (ZnCl₂ Separator) which extracted any Zinc Chloride from the stream. The purified stream was then sent to the raw methanol reactor.

The methanol reaction unit was composed of a mixer which collected the stream recycled after passing through the reactor and combined it in a mixer (Mixer-4) with the purified stream from the zinc oxide process. This mixed stream was then compressed (Compressor-1) to a higher pressure and cooled (Heat Exchanger-3) to a lower temperature meeting the reactor specifications. The reactor itself (Methanol Reactor) converted carbon dioxide, carbon monoxide, and hydrogen into methanol, carbon monoxide, and water. The resulting product streams were sent to a flash separator (MeOH Separator) which extracted the impure liquid stream of methanol and directed the remaining contents to a splitter (Splitter-2) where the stream was split into 3 streams: a waste stream (PURGE), a stream that was recycled in with the feed biomass, and the recycle stream for the methanol production unit.

The stream containing methanol was sent to a downstream distillation unit pictured on the lower part of Figure 3.3.1. This unit began by feeding the inlet stream to a methanol storage which

limited the amount of methanol fed to the distillation column. The purge gas stream coming out of it removed the carbon monoxide by permitting ventilation. The resulting methanol stream was sent through a pump (Pump-3) which powered the flow into the column. The column (MeOH Distillation Column) purified the methanol stream and collected the more volatile component, methanol, which was then condensed back to a liquid phase through the condenser.

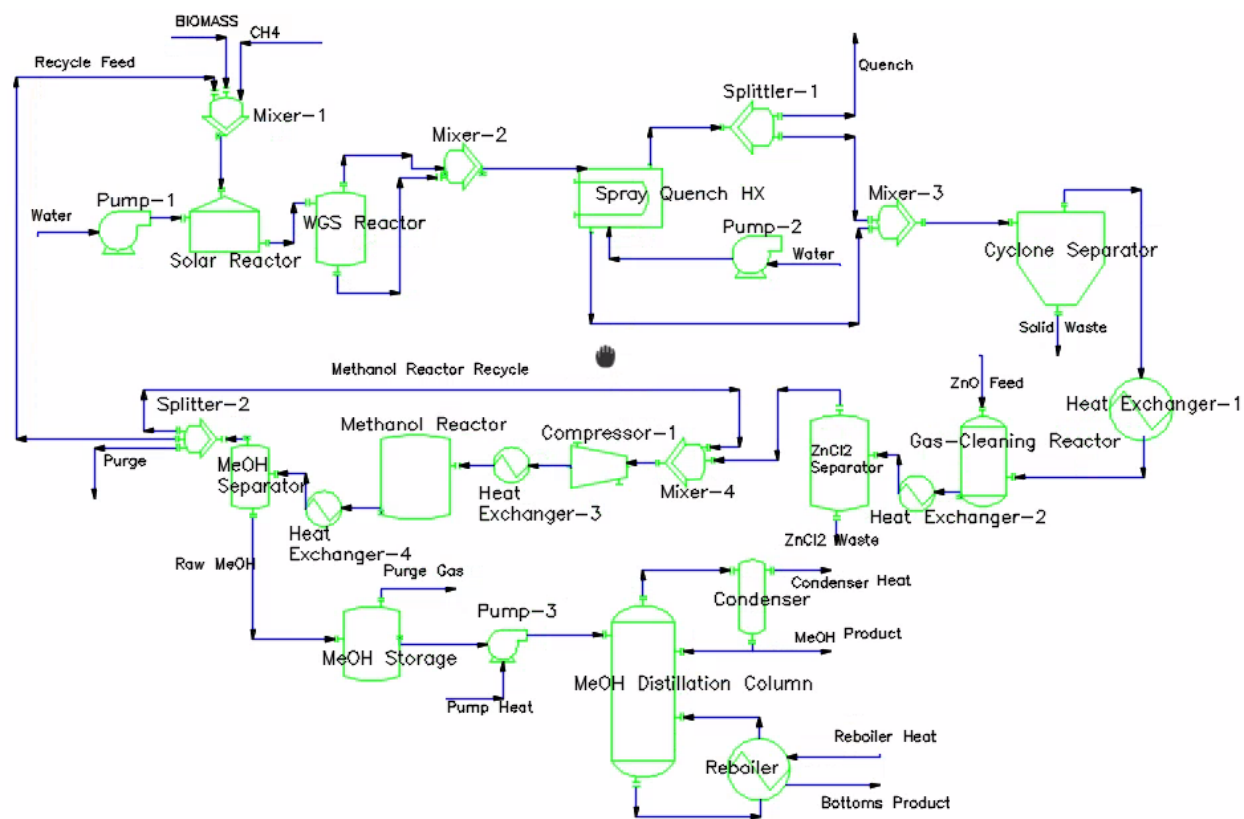


Figure 3.3.1 Process flow diagram

Table 3.3.1 Process Equipment Conditions

Equipment	Temperature (°C)	Pressure (bar)	Main Component(s) Produced for Further Processing
Solar Reactor	1450	35	CO, H ₂ , H ₂ S, HCl
WGS Reactor	800	35	H ₂ S, HCl, CO ₂ , H ₂ , CO
Spray Quench HX	N/A	N/A	H ₂ S, HCl, CO ₂ , H ₂
Cyclone Separator	N/A	N/A	H ₂ S, HCl, CO ₂ , H ₂ , H ₂ O, CO

Gas-Cleaning Reactor	650	35	ZnS, ZnCl ₂ , H ₂ O, H ₂ , CO, CO ₂
ZnCl ₂ Separator	650	35	H ₂ O, H ₂ , CO, CO ₂
Methanol Reactor	420	80	H ₂ O, H ₂ , CO, CO ₂ , CH ₃ OH
MeOH Separator	50	30	Top - H ₂ O, H ₂ , CO, CO ₂ Bottom - CH ₃ OH, CO
MeOH Storage	20	1.01	CH ₃ OH, CO
MeOH Distillation Column-Top Tray	86.5	2.28	CH ₃ OH
MeOH Distillation Column-Bottom Tray	73.7	1.42	Waste stream
Condenser	70.84	2.07	CH ₃ OH
Reboiler	77.96	1.624	Waste stream

3.4 Battery Limits

Below are the assumptions that were made in predicting the general operations of this plant.

- Plant Capacity: 56 million gallons per year of methanol
- There was no restriction in availability of material necessary for production such that no delays would be encountered in accumulating necessary quantities of reactants
- This design was a grass-roots project, built from scratch
- The location of this plant (excluding heliostat field) will be Long Beach, California
- The utilities chosen are easy to find and as such should be readily available
- This plant will be comprised of continuous processes, with the partial exception of the zinc oxide bed

Inside Battery Limits

Heliostat Field: Electricity will need to be provided towards the operations tower in this plant so that computers and transmitters are operational which will allow operators and engineers to make necessary adjustments. Water will need to be provided for drinking, sanitation, and disposal.

Reactors: Electricity will need to be provided towards these units so that specifications are revealed and transmitted appropriately and also so controls are operated correctly. Heat transfer fluid will need to be provided for appropriate cooling so that runaway reactions are avoided.

Heat Exchangers: Electricity will need to be provided towards these units so that specifications are revealed and transmitted appropriately and also so controls are operated correctly. Heat transfer fluid will need to be provided for appropriate cooling or heating so that process material meets specifications for further instrumentations.

Separators/Mixers: Electricity will need to be provided towards these units so that specifications are revealed and transmitted appropriately and also so controls are operated correctly.

Pumps: Electricity will need to be provided towards these units so that specifications are revealed and transmitted appropriately and also so controls are operated correctly.

Compressors: Electricity will need to be provided towards these units so that specifications are revealed and transmitted appropriately and also so controls are operated correctly.

Outside Battery Limits

We need to consider the storage and distribution of products, the economics of selling the product, facilities necessary to accommodate labor, facilities and equipment necessary to manage processes, facilities necessary to maintain operations, and facilities necessary to house transportation equipment.

Not all products were expected to be sold immediately upon production, so a storage process had to be established. Storage tanks will have to be manufactured for each product and waste byproduct according to the volume expected to accumulate throughout a given time period. These tanks will not be evenly sized as some products and waste byproducts will be produced in larger volumes than others. There needed to be an adequate amount of space between each of these tanks not only so that safety specifications were met but also so that loading and unloading of product could be performed. Therefore, a road network needed to be established throughout the plant so that storage tanks and equipment could be reached with relatively large automobiles (up to the size of a firetruck).

Facilities needed to be installed to accommodate operators, such as cafeterias, locker rooms, offices, meeting rooms. Operating rooms and operating towers were planned to be installed on site so that processes could be managed. Structures such as ladders and walkways will need to be installed around equipment so that operators are able to access and make adjustments to units when needed. Facility and/or land will need to be modified and construction performed so that automobiles such as cranes or trucks can be stored nearby for necessary use.

3.5 Material Balance

In designing the various reactors and other required equipment for this system, it was critical to gain an initial understanding of the scale and feed flows required for the process. The problem

statement stated that 56 million gallons of methanol must be produced over the 2920 operational hours of this system per year. Due to the presence of phase changes throughout the production process, the first step was to convert this volumetric rate in units of gallons per year to a more usable molar flow rate. This conversion is given below:

$$56 \text{ M} \frac{\text{Gallon MeOH}}{\text{year}} \left(\frac{3.78541 \text{ L}}{1 \text{ US Gallon}} \right) \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) \left(\frac{792 \text{ kg}}{\text{m}^3} \right) \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol}}{32.04 \text{ g}} \right) = 5.24 * 10^9 \frac{\text{mol}}{\text{year}} \text{ MeOH}$$

Accordingly, it was also necessary to convert the weight fractions of biomass into mole fractions, putting everything on a molar basis prior to calculations. Molecular weights were known for all components in the biomass, making the conversion straightforward and expressed by the form:

$$\left(\frac{n}{N} \right)_i = \frac{\left(\frac{m}{M} \right)_i / MW_i}{\sum_i \left(\frac{m}{M} \right)_i / MW_i} \quad (3.5.1)$$

In this equation, $\left(\frac{n}{N} \right)_i$ represented the mole fraction of component i, $\left(\frac{m}{M} \right)_i$ represented the mass fraction of component i, and MW_i was the molar mass of component i. A table of the biomass component breakdown, including both mass and mole fractions, is included below in Table 3.5.1.

Table 3.5.1 Biomass Component Breakdown

Component	Weight Fraction	Molar Mass (g/mol)	Mole Fraction
Cellulose	0.6825	162.1436	0.5623
Lignin	0.2175	180.2045	0.1612
Ash	0.0878	60.086	0.1952
N	0.0061	14.007	0.0582
S	0.0001	32.065	0.0004
Cl	0.006	35.453	0.0226
Sum	1	--	1

An overall molecular weight was also calculated for the biomass, so that the molar flow of biomass determined over the course of the material balances could be converted back to a mass flow rate. The overall molecular weight was calculated as a molar weighted average of the component molecular weights, with the following formula, with $\left(\frac{n}{N} \right)_i$ defined as above:

$$\text{Biomass MW} = \sum_i MW_i * \left(\frac{n}{N}\right)_i \quad (3.5.2)$$

Using this formula, the biomass molecular weight was calculated as 133.60 grams per mole.

In order to establish the amount of reactants required to produce the required amount of methanol in a year, material balances were performed for each of the reactions performed in the overall process. The reactants for which annual flow rates were determined were biomass, water, and methane gas. Working from the beginning, the amount of each molecule that was produced or consumed in the reaction series was determined based on the stoichiometric coefficients and given conversions for each reactor. For ease, these were divided into groupings based upon the various reactors.

The first set of reactions occurred in the Solar Thermal Gasification reaction, and are included as follows with the corresponding conversions:

1. $C_6H_{10}O_5 + H_2O \rightarrow 6 CO + 6 H_2$ Conversion: 100% conversion of cellulose
2. $C_{10}H_{12}O_3 + 7 H_2O \rightarrow 10 CO + 13 H_2$ Conversion: 100% conversion of lignin
3. $S + H_2 \rightarrow H_2S$ Conversion: 100% conversion of S
4. $Cl_2 + H_2 \rightarrow 2 HCl$ Conversion: 100% conversion of Cl_2
5. $CH_4 + H_2O \rightarrow CO + 3 H_2$ Conversion: 100% conversion of CH_4

For this reactor, the calculations took the following form, with the equations provided in the table below. Positive coefficients meant that the component was produced in the reaction, where negative coefficients suggested that the component was consumed.

Table 3.5.2 Solar Thermal Gasification Reaction Correlations

Component	Initial (mol/yr)	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5	Final (mol/yr)
Cellulose	0.5623*Bio mass Flow	-1*Initial Cellulose	0	0	0	0	Sum Initial + Reactions 1-5
H ₂ O	H ₂ O Flow	-1* Initial Cellulose	-7*Initial Lignin	0	0	-1*Initial Methane	Sum Initial + Reactions 1-5
CO	0	6* Initial Cellulose	10*Initial Lignin	0	0	1*Initial Methane	Sum Initial + Reactions 1-5
H ₂	0	6* Initial	13*Initial	-1*Initial S	-(1/2)*Initial	3*Initial	Sum Initial

		Cellulose	Lignin		Cl	Methane	+ Reactions 1-5
Lignin	0.1612*Bio mass Flow	0	-1* Initial Lignin	0	0	0	Sum Initial + Reactions 1-5
S	0.0004*Bio mass Flow	0	0	-1*Initial S	0	0	Sum Initial + Reactions 1-5
H ₂ S	0	0	0	1*Initial S	0	0	Sum Initial + Reactions 1-5
Cl	0.0226*Bio mass Flow	0	0	0	-1*Initial Cl	0	Sum Initial + Reactions 1-5
HCl	0	0	0	0	1*Initial Cl	0	Sum Initial + Reactions 1-5
CH ₄	CH ₄ Flow	0	0	0	0	-1*Initial Methane	Sum Initial + Reactions 1-5

The next set of reactions that occurred in the process of methanol production was a water-gas shift reaction, which occurred on the existing stream from the solar reactor. The conversion of this reaction was not given directly. Instead, an ideal ratio of hydrogen gas to carbon monoxide gas following this shift was provided. Ideally, a hydrogen to carbon monoxide ratio should be very nearly two. Callaghan et. al. suggested that the conversion of carbon dioxide for this reaction should be kept to 15% or less^[3.5]. Accordingly, for the sake of these material balances, an extent of reaction of 0.15 was utilized. The water-gas shift reaction had the following form:



Similar to the solar thermal gasification reaction, the syngas balance reaction could be calculated through coefficient correlations as outlined in Table 3.5.3.

Table 3.5.3 Syngas Reaction Correlations

Component	Initial b (mol/yr)	Reaction	Final b (mol/yr)
CO	Final CO Flow from Solar Thermal Reactor	-0.15*Initial (b) CO	Sum Initial b + Reaction
H ₂ O	Final Water Flow from Solar Thermal Reactor	-0.15* Initial (b) CO	Sum Initial b + Reaction
CO ₂	0	0.15* Initial (b) CO	Sum Initial b + Reaction

H ₂	Final H ₂ Flow from Solar Thermal Reactor	0.15* Initial (b) CO	Sum Initial b + Reaction
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While not a direct step in the process of methanol production, a zinc oxide bed was also included as part of this process for the purpose of converting the portion of hydrochloric acid and hydrogen sulfide to water and solid precipitates. Due to the effect this had on the overall amount of water present in the system, this reactor was also included in the reaction pathway. The reactions occurring in the zinc oxide reactor were as follows:

1. $ZnO + H_2S \rightarrow ZnS + H_2O$ Conversion: 100% conversion of H₂S
2. $ZnO + 2 HCl \rightarrow ZnCl_2 + H_2O$ Conversion: 100% conversion of HCl

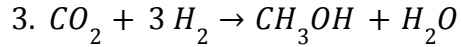
It was worth noting that solid zinc oxide was also required for the performance of this reaction. Due to zinc oxide only occurring in this stage of the process, it was assumed that all the zinc oxide was consumed in the two reactions and therefore the amount required annually was retroactively calculated based upon what would be required for 100% conversion. The correlations for this reactor are given in Table 3.5.4.

Table 3.5.4 Zinc Oxide Bed Reaction Correlations

Component	Initial c (mol/yr)	Reaction 1	Reaction 2	Final c (mol/yr)
ZnO	Sum Reactions 1 and 2	-1*Initial (c) H ₂ S	-(1/2)* Initial (c) HCl	0
H ₂ S	Final H ₂ S Flow from Solar Thermal Reactor	-1*Initial (c) H ₂ S	0	Sum Initial c + Reactions 1-2
ZnS	Final ZnS Flow from Solar Thermal Reactor	1*Initial (c) H ₂ S	0	Sum Initial c + Reactions 1-2
H ₂ O	Final b Water Flow from Syngas Reaction	-1*Initial (c) H ₂ S	-(1/2)* Initial (c) HCl	Sum Initial c + Reactions 1-2
HCl	Final HCl Flow from Solar Thermal Reactor	0	-1* Initial (c) HCl	Sum Initial c + Reactions 1-2
ZnCl ₂	0	0	(1/2)* Initial (c) HCl	Sum Initial c + Reactions 1-2

The final step in this process was the actual production of methanol. This occurred in the methanol production reactor, which contained three reactions, as follows.

1. $CO_2 + H_2 \rightarrow CO + H_2O$ Conversion: 45% conversion of CO₂
2. $CO + 2 H_2 \rightarrow CH_3OH$ Conversion: 45% conversion of CO



Conversion: 45% conversion of CO_2

In order to perform a material balance, it was assumed that the reactions did not proceed simultaneously but instead occurred in sequence. The reason for this assumption was that the conversions of some of the reactions were put in terms of species which were being produced in other reactions. For the stoichiometric correlations to work as a method, it was assumed that the reactions were sequential. For a more visual representation of this, the correlation equations have been provided in Table 3.5.5.

Table 3.5.5 Methanol Production Reaction Correlations

Component	Initial d (mol/yr)	Reaction 1	Reaction 2	Reaction 3	Final d (mol/yr)
CO_2	Final b CO_2 Flow from Syngas Reaction	$-0.45 \cdot \text{Initial (d) CO}_2$	0	$-0.45 \cdot \text{Sum (Initial (d) CO}_2 + \text{Reaction 1 CO}_2 + \text{Reaction 2 CO}_2)$	Sum Initial d + Reactions 1-3
H_2	Final b H_2 Flow from Syngas Reaction	$-0.45 \cdot \text{Initial (d) CO}_2$	$-0.45 \cdot 2 \cdot \text{Sum (Initial (d) CO} + \text{Reaction 1 CO})$	$-0.45 \cdot 3 \cdot \text{Sum (Initial (d) CO}_2 + \text{Reaction 1 CO}_2 + \text{Reaction 2 CO}_2)$	Sum Initial d + Reactions 1-3
CO	Final b CO Flow from Syngas Reaction	$0.45 \cdot \text{Initial (d) CO}_2$	$-0.45 \cdot \text{Sum (Initial (d) CO} + \text{Reaction 1 CO})$	0	Sum Initial d + Reactions 1-3
H_2O	Final c Water Flow from Zinc Oxide Bed	$0.45 \cdot \text{Initial (d) CO}_2$	0	$-0.45 \cdot \text{Sum (Initial (d) CO}_2 + \text{Reaction 1 CO}_2 + \text{Reaction 2 CO}_2)$	Sum Initial d + Reactions 1-3
CH_3OH	0	0	$0.45 \cdot \text{Sum (Initial (d) CO} + \text{Reaction 1 CO})$	$-0.45 \cdot \text{Sum (Initial (d) CO}_2 + \text{Reaction 1 CO}_2 + \text{Reaction 2 CO}_2)$	Sum Initial d + Reactions 1-3

Once these correlations had been established and set up, Excel's solver tool was used to find the annual quantities of biomass, water, and methane that would result in the annual methanol production calculated at the beginning of this process: $5.24 \cdot 10^9$ moles of methanol per year. (The Excel spreadsheet with this initial solver solution, set up as shown above, can be referenced in Appendix A.) Simultaneously, Excel solver ensured that the syngas ratio of hydrogen gas to carbon monoxide was 2. Due to the low conversion of carbon monoxide in the equilibrium syngas reaction, it was necessary to add more methane to achieve this desired ratio. Methane was reacted in the solar thermal gasification reactor with water to form three moles of hydrogen for each mole of methane. This allowed the high concentration of hydrogen gas necessary to attain the desired ratio while keeping conversion of carbon monoxide in the water-gas shift reaction low to avoid production of carbon dioxide.

When a Solver solution had been obtained, the possibility of the results was confirmed by checking to ensure that none of the “Final” values obtained via the correlations in the tables above were negative. A negative value would imply that more of that species had been produced than had initially been present, an impossibility that would have violated the law of conservation of mass.

From the material balance equations, it was determined that in order to produce the desired quantity of 5.24×10^9 moles of methanol per year, this system would require 1.78×10^9 moles of biomass per year, 7.53×10^9 moles per year of water, and 2.78×10^9 moles per year of biomass. 2.08×10^7 moles per year of solid zinc oxide will also be required for the zinc oxide bed reactor.

The reactors included in this material balance operated 8 hours per day, 365 days per year, for a total of 2920 hours per year. Based upon this, hourly flow rates (with the hours only representing operational hours) could also be determined. The inlet flow rates into the system were at least 608.61 kmols/hr of biomass, 2580.39 kmols/hr of water, 953.02 kmol/hr of methane, and 7.13 kmol/hr of solid zinc oxide. The ratios of these inlet reactant flow rates were also compared. For each mole of biomass introduced into the system, approximately $4 \frac{1}{4}$ moles of water and $1 \frac{1}{2}$ moles of methane had to be introduced as well. Each mole of biomass introduced to the system produced around 3 moles of methanol. Additionally, each mole of solid zinc oxide in the zinc oxide bed reactor accounted for the hydrogen sulfide and hydrochloric acid byproducts from around $85 \frac{1}{2}$ moles of biomass. A complete summary of the inlet flow rates in both moles per hour and mass per hour is provided in Table 3.5.6.

Table 3.5.6 Feed Flow Rates for All Components From Initial Mass Balances

Component	Molar Flow Rate (kmol/hr)	Mass Flow Rate (kg/hr)
Biomass	608.61	81,308.08
Cellulose	342.24	55,492.76
Lignin	98.14	17,684.51
Ash	118.81	7,138.85
N	35.41	495.98
S	0.25	8.13
Cl	13.76	487.85
Methane	953.02	15,286.44
Water	2580.39	46,498.66

ZnO	7.13	580.55
-----	------	--------

When modeling the series of reactors in Aspen, recycle streams were added. This consisted of both an overall recycle stream, as well as a recycle stream around the methanol reactor specifically. These recycle streams increased the production of methanol, as recycling the reactants through the methanol reactor (where they achieved only 45% conversion on each pass) resulted in a higher overall conversion of reactants to methanol and byproducts. In attempting to get Aspen to converge with the recycle streams present, it was necessary to modify some of the streams slightly. The flow rate of methane into the system was increased to 2570 kmol/hr, and the inlet water flow rate was increased to 3600 kmol/hr. The increase in flow rate was necessary, also, as the water gas shift reactor in Aspen achieved a much lower conversion of carbon monoxide than was found in the literature and applied to the initial mass balances.

The combination of the reduced conversion of carbon monoxide in the water gas shift reaction and the increased production of methanol due to the recycle streams resulted in an overall production of methanol that was much greater than required. As there was no need for overproduction of methanol without an additional purchaser, this allowed for a reduction in the requirements of the inlet feed streams, and optimization was performed in order to produce a value as close as possible to the required 56 million gallons. Producing 1812 kmol/hr of methanol (56.5 million gallons per year) required feed streams of 192.73 kmol/hr of biomass, 848.1 kmol/hr of methane, 1188.0 kmol/hr of water, and 2.35 kmol/hr. The full table of inlet flow rates is given in Table 3.5.7.

Table 3.5.7 Feed Flow Rates for All Components From Final Aspen Simulation

Component	Molar Flow Rate (kmol/hr)	Mass Flow Rate (kg/hr)
Biomass	192.73	26,831.7
Cellulose	112.94	18,312.4
Lignin	32.39	5,836.14
Ash	39.21	2,355.81
N ₂	5.84	163.72
S	0.08	2.65
Cl ₂	2.27	160.98
Methane	848.1	13,605.9
Water	1188.0	21,402.2

ZnO	2.35	191.50
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With the values from the simulation, rather than the earlier mass balances, the ratios of the inlet reactants were also affected. For each mole of biomass introduced into the system, approximately 6.2 moles of water and 4.4 moles of methane had to be introduced as well. Each mole of biomass introduced to the system produced around 9.4 moles of methanol. Additionally, each mole of solid zinc oxide in the zinc oxide bed reactor accounted for the hydrogen sulfide and hydrochloric acid byproducts from around 82 moles of biomass. These new values were utilized rather than those from the initial mass balance for the remainder of the design of this methanol production process.

3.6 Energy Balances

In initially finding the amount of energy required for the solar reactor, the amounts of biomass, methanol, and steam fed to the reactor were taken from the material balances. A summary of the calculations was provided in this section, but the calculations performed in Excel could be referenced in full in Appendix B. All reactions in the solar thermal reactor were assumed to go to 100 percent conversion. The solar thermal reactor was fed with biomass, methanol, and water and the following reactions were carried out:



Each of these reactions were performed at 1450 °C in the reactor. Since properties such as heat of combustions were known at 25 °C, a reaction temperature shift had to be carried out for each reaction from 25 °C to 1450 °C via heat capacity integrations. Heat capacity constants and heats of combustion, when applicable, for each species were found through available literature^[3.6.1] and applied towards these calculations.

3.6.1 Cellulose ΔH_r at 25 °C:

Beginning with the cellulose reaction, summed heats of combustions were calculated, that is, reactants minus products on a mole-ratio basis to determine the heat of reaction at 25 °C.

$$\begin{aligned}
 \Delta H_{r,25} &= \Delta H_{C, \text{Reactants}} - \Delta H_{C, \text{Products}} \\
 &= \sum n \Delta H_{C, \text{Reactants}} - \sum n \Delta H_{C, \text{Products}} \\
 &= \Delta H_{C, C_6H_{10}O_5} + \Delta H_{C, H_2O} - 6\Delta H_{C, CO} - 6\Delta H_{C, H_2} \\
 &= (-17340 \frac{J}{g})(162.14 \frac{g}{mol})(\frac{1 kJ}{1000 J}) + 0 - 6(-282.99 \frac{kJ}{mol})
 \end{aligned} \tag{3.6.1.1}$$

$$\begin{aligned}
& - 6 \left(- 285.84 \frac{\text{kJ}}{\text{mol}} \right) \\
& = 601.47 \frac{\text{kJ}}{\text{mol}}
\end{aligned}$$

3.6.2 Cellulose ΔH_r at 1450 °C:

To find the heat of reaction at 1450 °C for this cellulose species, reactants cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$) and water had to be cooled (negatively integrated) from 1450 °C to 25 °C based on the heat capacity constants found. The products, carbon monoxide (CO) and hydrogen (H_2) had to be heated (positively integrated) from 25 °C to 1450 °C based on their respective heat capacity constants. Using these products along with the heat of reaction at 25 °C in section 3.6.2, the heat of reaction at 1450 °C was determined.

Energy required to create necessary temperature changes:

$$\begin{aligned}
\Delta H_{\text{Cellulose}} &= - \int_{25}^{1450} n_i \cdot (11704 \cdot 10^{-6} + 672 \cdot 10^{-6} \cdot T) dt \quad (3.6.2.1) \\
&= -1 (\text{mol}) \cdot [(11704 \cdot 10^{-6} \cdot T + 336.03 \cdot 10^{-6} \cdot T^2)_{T=1450\text{C}} - (11704 \cdot 10^{-6} \cdot T + 336.03 \cdot 10^{-6} \cdot T^2)_{T=25\text{C}}] \\
&= -(\text{mol}) \cdot (977.60 (\text{kJ/mol}) - 26.38 (\text{kJ/mol})) \\
&= -951.22 \text{ kJ/mol}
\end{aligned}$$

$$\begin{aligned}
\Delta H_{\text{H}_2\text{O},(\text{l})} &= - \int_{25}^{242.6} n_{\text{H}_2\text{O}} \cdot C_{p,\text{H}_2\text{O}} \cdot dT \quad (3.6.2.2) \\
&= -n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25\text{C},i} \right] \\
&= -1 (\text{mol}) \cdot (18.29 (\text{kJ/mol}) - 1.89 (\text{kJ/mol})) \\
&= -16.41 \text{ kJ}
\end{aligned}$$

$$\begin{aligned}
\Delta H_{\text{vap}} &= -1 (\text{mol}) \cdot 1752.84 \frac{\text{J}}{\text{g}} \cdot 1000^{-1} \frac{\text{kJ}}{\text{J}} \cdot 18 \frac{\text{g}}{\text{mol}} \quad (3.6.2.3) \\
&= -31.55 (\text{kJ})
\end{aligned}$$

$$\begin{aligned}
\Delta H_{\text{H}_2\text{O},(\text{g})} &= - \int_{242.6}^{1450} n_{\text{H}_2\text{O}} \cdot C_{p,\text{H}_2\text{O}} \cdot dT \quad (3.6.2.4) \\
&= -n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25\text{C},i} \right] \\
&= -1 (\text{mol}) \cdot (59.51 (\text{kJ/mol}) - 8.35 (\text{kJ/mol})) \\
&= -51.15 (\text{kJ})
\end{aligned}$$

$$\begin{aligned}
\Delta H_{\text{CO}} &= \int_{25}^{1450} n_{\text{CO}} \cdot C_{p,\text{CO}} \cdot dT \quad (3.6.2.5) \\
&= n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25\text{C},i} \right]
\end{aligned}$$

$$\begin{aligned}
&= 6 \text{ (mol)} \cdot (47.45 \text{ (kJ/mol)} - 0.73 \text{ (kJ/mol)}) \\
&= 280.35 \text{ (kJ)}
\end{aligned}$$

$$\begin{aligned}
\Delta H_{H_2} &= \int_{25}^{1450} n_{H_2} \cdot C_{p,H_2} \cdot dT \quad (3.6.2.6) \\
&= n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450, C, i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25, C, i} \right] \\
&= 6 \text{ (mol)} \cdot (44.28 \text{ (kJ/mol)} - 0.72 \text{ (kJ/mol)}) \\
&= 261.34 \text{ (kJ)}
\end{aligned}$$

Heat of Reaction of Cellulose at 1450 °C:

$$\begin{aligned}
\Delta H_{r, 1450} &= \sum_{1450}^{25} n C_{P, reactant} dT + \Delta H_{r, 25} + \sum_{25}^{1450} n C_{P, product} dT \quad (3.4.2.7) \\
&= \Delta H_{cellulose} + \Delta H_{H_2O, (l)} + \Delta H_{H_2O, vap} + \Delta H_{H_2O, (g)} + \Delta H_{r, 25} + \Delta H_{CO} + \Delta H_{H_2} \\
&= (-951.22 - 16.407 - 31.55 - 51.15 + 601.47 + 280.35 + 261.34) \frac{kJ}{mol} \\
&= 92.83 \frac{kJ}{mol}
\end{aligned}$$

3.6.3 Lignin ΔH_r at 25 °C:

The same process shown in 3.6.1 was used again, this time for lignin. The summed heats of combustions were calculated, ie. reactants minus products on a mole-ratio basis, to determine the heat of reaction at 25 °C. The energy required to raise the temperature of the products and to lower the temperature of the reactants was then added to the heat of reaction at 25 °C to find the heat of reaction at 1450 °C.

$$\begin{aligned}
\Delta H_{r, 25} &= \Delta H_{C, Reactants} - \Delta H_{C, Products} \quad (3.6.3.1) \\
&= \sum n \Delta H_{C, Reactants} - \sum n \Delta H_{C, Products} \\
&= \Delta H_{C, C_6H_{10}O_5} + 7\Delta H_{C, H_2O} - 10\Delta H_{C, CO} - 13\Delta H_{C, H_2} \\
&= (-21178 \text{ J/g}) \cdot 180.21 \frac{g}{mol} \cdot \frac{1 \text{ kJ}}{1000 \text{ J}} + 7 \cdot 0 - 10 \cdot (-282.99 \frac{kJ}{mol}) \\
&\quad - 13 \cdot (-285.84 \frac{kJ}{mol}) \\
&= 2729.33 \frac{kJ}{mol}
\end{aligned}$$

3.6.4 Lignin ΔH_r at 1450 °C:

The process here was the same as in 3.6.2 with a single difference in that this was for the lignin reaction as opposed to the cellulose reaction.

Energy required to create necessary temperature changes:

$$\begin{aligned}
 \Delta H_{\text{lignin}} &= - \int_{25}^{1450} n_i \cdot (31431.7 \cdot 10^{-6} + 394.427 \cdot 10^{-6} T) dt & (3.6.4.1) \\
 &= -1 \text{ (mol)} \cdot [(31431.7 \cdot 10^{-6} \cdot T + 197.21 \cdot 10^{-6} \cdot T^2)_{T=1450\text{C}} - (31431.7 \cdot 10^{-6} \cdot T + 197.21 \cdot 10^{-6} \cdot T^2)_{T=25\text{C}}] \\
 &= -(\text{mol}) \cdot (639.7 \text{ (KJ/mol)} - 26.9 \text{ (KJ/mol)}) \\
 &= -612.83 \text{ (kJ/mol)}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{\text{H}_2\text{O},(\text{l})} &= - \int_{25}^{242.6} n_{\text{H}_2\text{O}} \cdot C_{\text{p,H}_2\text{O}} \cdot dT & (3.6.4.2) \\
 &= -n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25\text{C},i} \right] \\
 &= -7 \text{ (mol)} \cdot (18.29 \text{ (kJ/mol)} - 1.89 \text{ (kJ/mol)}) \\
 &= -114.84 \text{ (kJ)}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{\text{vap}} &= -7 \text{ (mol)} \cdot 1752.84 \frac{\text{J}}{\text{g}} \cdot 1000^{-1} \frac{\text{kJ}}{\text{J}} \cdot 18 \frac{\text{g}}{\text{mol}} & (3.6.4.3) \\
 &= -220.86 \text{ (kJ)}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{\text{H}_2\text{O},(\text{g})} &= - \int_{242.6}^{1450} n_{\text{H}_2\text{O}} \cdot C_{\text{p,H}_2\text{O}} \cdot dT & (3.6.4.4) \\
 &= -n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25\text{C},i} \right] \\
 &= -7 \text{ (mol)} \cdot (59.51 \text{ (kJ/mol)} - 8.35 \text{ (kJ/mol)}) \\
 &= -358.07 \text{ (kJ)}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{\text{CO}} &= \int_{25}^{1450} n_{\text{CO}} \cdot C_{\text{p,CO}} \cdot dT & (3.6.4.5) \\
 &= n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25\text{C},i} \right] \\
 &= 10 \text{ (mol)} \cdot (47.45 \text{ (kJ/mol)} - 0.73 \text{ (kJ/mol)}) \\
 &= 467.25 \text{ (kJ)}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{\text{H}_2} &= \int_{25}^{1450} n_{\text{H}_2} \cdot C_{\text{p,H}_2} \cdot dT & (3.6.4.6) \\
 &= n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25\text{C},i} \right] \\
 &= 13 \text{ (mol)} \cdot (44.28 \text{ (kJ/mol)} - 0.72 \text{ (kJ/mol)}) \\
 &= 566.25 \text{ (kJ)}
 \end{aligned}$$

Heat of Reaction of Lignin at 1450 °C:

$$\begin{aligned}
 \Delta H_{r, 1450} &= \sum_{1450}^{25} nC_{P, reactant} dT + \Delta H_{r, 25} + \sum_{25}^{1450} nC_{P, product} dT \quad (3.6.4.7) \\
 &= \Delta H_{lignin} + \Delta H_{H_2O(l)} + \Delta H_{H_2O, vap} + \Delta H_{H_2O(g)} + \Delta H_{r, 25} + \Delta H_{CO} + \Delta H_{H_2} \\
 &= (-612.83 - 114.85 - 220.86 - 358.07 + 2729.33 + 467.25 + 566.25) \frac{kJ}{mol} \\
 &= 2456.22 \frac{kJ}{mol}
 \end{aligned}$$

3.6.5 Methane ΔH_r at 25 °C:

The same process as 3.6.1 and 3.6.3 was utilized here for the methane reaction at 25°C.

$$\begin{aligned}
 \Delta H_{r, 25} &= \Delta H_{C, Reactants} - \Delta H_{C, Products} \quad (3.6.5.1) \\
 &= \sum n \Delta H_{C, Reactants} - \sum n \Delta H_{C, Products} \\
 &= \Delta H_{C, CH_4} + \Delta H_{C, H_2O} - \Delta H_{C, CO} - 3 \Delta H_{C, H_2} \\
 &= (-890.36 \frac{kJ}{mol}) + 1 \cdot 0 - (-282.99 \frac{kJ}{mol}) - 3 \cdot (-285.84 \frac{kJ}{mol}) \\
 &= 250.15 \frac{kJ}{mol}
 \end{aligned}$$

3.6.6 Methane ΔH_r at 1450 °C:

The process here was the same as in 3.6.2 and 3.6.4 with a single difference in that this is for the methane reaction.

Energy required to create necessary temperature changes:

$$\begin{aligned}
 \Delta H_{CH_4} &= - \int_{25}^{1450} n_{CH_4} \cdot C_{p, CH_4} \cdot dT \quad (3.6.6.1) \\
 &= -n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25} \right] \\
 &= -1 \text{ (mol)} \cdot (98.81 \text{ kJ/mol} - 0.87 \text{ kJ/mol}) \\
 &= -97.93 \text{ (kJ)}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{H_2O(l)} &= - \int_{25}^{242.6} n_{H_2O} \cdot C_{p, H_2O} \cdot dT \quad (3.6.6.2) \\
 &= -n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=242.6} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25} \right] \\
 &= -1 \text{ (mol)} \cdot (18.29 \text{ (kJ/mol)} - 1.89 \text{ (kJ/mol)}) \\
 &= -16.41 \text{ (kJ)}
 \end{aligned}$$

$$\Delta H_{\text{vap}} = -1 \text{ (mol)} \cdot 1752.84 \frac{\text{J}}{\text{g}} \cdot 1000 \frac{\text{g}}{\text{mol}} \cdot 18 \frac{\text{g}}{\text{mol}} \quad (3.6.6.3)$$

$$= -31.55 \text{ (kJ)}$$

$$\Delta H_{\text{H}_2\text{O},(\text{g})} = - \int_{242.6}^{1450} n_{\text{H}_2\text{O}} \cdot C_{\text{p,H}_2\text{O}} \cdot dT \quad (3.6.6.4)$$

$$= -n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25} \right]$$

$$= -1 \text{ (mol)} \cdot (59.51 \text{ (kJ/mol)} - 8.35 \text{ (kJ/mol)})$$

$$= -51.15 \text{ (kJ)}$$

$$\Delta H_{\text{CO}} = \int_{25}^{1450} n_{\text{CO}} \cdot C_{\text{p,CO}} \cdot dT \quad (3.6.6.5)$$

$$= n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25} \right]$$

$$= 1 \text{ (mol)} \cdot (47.45 \text{ (kJ/mol)} - 0.73 \text{ (kJ/mol)})$$

$$= 43.56 \text{ (kJ)}$$

$$\Delta H_{\text{H}_2} = \int_{25}^{1450} n_{\text{H}_2} \cdot C_{\text{p,H}_2} \cdot dT \quad (3.6.6.6)$$

$$= n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25} \right]$$

$$= 3 \text{ (mol)} \cdot (44.28 \text{ (kJ/mol)} - 0.72 \text{ (kJ/mol)})$$

$$= 130.67 \text{ (kJ)}$$

Heat of Reaction of Methane at 1450 °C:

$$\Delta H_{r, 1450} = \sum_{1450}^{25} n C_{P, \text{reactant}} dT + \Delta H_{r, 25} + \sum_{25}^{1450} n C_{P, \text{product}} dT \quad (3.6.6.7)$$

$$= \Delta H_{\text{CH}_4} + \Delta H_{\text{H}_2\text{O}} + \Delta H_{r, 25} + \Delta H_{\text{CO}} + \Delta H_{\text{H}_2}$$

$$= (-97.93 - 16.407 - 31.55 - 51.15 + 250.15 + 43.56 + 130.67) \frac{\text{kJ}}{\text{mol}}$$

$$= 230.50 \frac{\text{kJ}}{\text{mol}}$$

3.6.7 Total Energy Requirement:

With the heats of reaction at the proper temperature it was possible to solve for the total energy requirement. Equation (3.6.7.8) was helpful for showing what was needed. The heat required for the reactor could be taken as a sum of the heats required to heat up the reactants to 1450 °C, accommodate any phase changes, and the heat change due to the reactions.

Heat Required from Heating and Vaporizing Reactants to 1450 °C:

$$\begin{aligned}
 \Delta H_{\text{Cellulose}} &= \int_{25}^{1450} n_i \cdot (-11704 \cdot 10^{-6} + 672 \cdot 10^{-6} \cdot T) dt \\
 &= 3.42 \cdot 10^5 \text{ (mol/hr)} \cdot [(-11704 \cdot 10^{-6} \cdot T + 336.03 \cdot 10^{-6} \cdot T^2)_{T=1450\text{C}} \\
 &\quad - (-11704 \cdot 10^{-6} \cdot T + 336.03 \cdot 10^{-6} \cdot T^2)_{T=25\text{C}}] \\
 &= 3.42 \cdot 10^5 \text{ (mol/hr)} \cdot (977.6 \text{ (kJ/mol)} - 26.38 \text{ (kJ/mol)}) \\
 &= 3.26 \cdot 10^8 \text{ (kJ/hr)}
 \end{aligned} \tag{3.6.7.1}$$

$$\begin{aligned}
 \Delta H_{\text{lignin}} &= \int_{25}^{1450} n_i \cdot (31431.7 \cdot 10^{-6} + 394.427 \cdot 10^{-6} \cdot T) dt \\
 &= 9.84 \cdot 10^4 \text{ (mol/hr)} \cdot [(31431.7 \cdot 10^{-6} \cdot T + 197.21 \cdot 10^{-6} \cdot T^2)_{T=1450\text{C}} \\
 &\quad - (31431.7 \cdot 10^{-6} \cdot T + 197.21 \cdot 10^{-6} \cdot T^2)_{T=25\text{C}}] \\
 &= 9.84 \cdot 10^4 \text{ (mol/hr)} \cdot (639.7 \text{ (kJ/mol)} - 26.9 \text{ (kJ/mol)}) \\
 &= 6.01 \cdot 10^7 \text{ (kJ/hr)}
 \end{aligned} \tag{3.6.7.2}$$

$$\begin{aligned}
 \Delta H_{\text{H}_2\text{O},1} &= \int_{25}^{242.6} n_{\text{H}_2\text{O}} \cdot C_{p,\text{H}_2\text{O}} \cdot dT \\
 &= -n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=242.6\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25\text{C},i} \right] \\
 &= 2.58 \cdot 10^6 \text{ (mol/hr)} \cdot (18.29 \text{ (kJ/mol)} - 1.89 \text{ (kJ/mol)}) \\
 &= 4.23 \cdot 10^7 \text{ (kJ/hr)}
 \end{aligned} \tag{3.6.7.3}$$

$$\begin{aligned}
 \Delta H_{\text{vap}} &= 2.58 \cdot 10^6 \text{ mol/hr} \cdot 1752.84 \text{ kJ/kg} \cdot 1 \text{ kg/1000g} \cdot 18 \text{ g/mol} \\
 &= 8.14 \cdot 10^7 \text{ (kJ/hr)}
 \end{aligned} \tag{3.6.7.4}$$

$$\begin{aligned}
 \Delta H_{\text{H}_2\text{O},2} &= \int_{242.6}^{1450} n_{\text{H}_2\text{O}} \cdot C_{p,\text{H}_2\text{O}} \cdot dT \\
 &= n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=242.6\text{C},i} \right] \\
 &= 2.58 \cdot 10^6 \text{ (mol/hr)} \cdot (59.51 \text{ (kJ/mol)} - 8.35 \text{ (kJ/mol)}) \\
 &= 1.32 \cdot 10^8 \text{ (kJ/hr)}
 \end{aligned} \tag{3.6.7.5}$$

$$\begin{aligned}
 \Delta H_{\text{CH}_4} &= \int_{25}^{1450} n_{\text{CH}_4} \cdot C_{p,\text{CH}_4} \cdot dT \\
 &= n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=1450\text{C},i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=242.6\text{C},i} \right] \\
 &= 9.53 \cdot 10^5 \text{ (mol/hr)} \cdot (98.81 \text{ (kJ/mol)} - 0.87 \text{ (kJ/mol)}) \\
 &= 9.33 \cdot 10^7 \text{ (kJ/hr)}
 \end{aligned} \tag{3.6.7.6}$$

$$\begin{aligned}
\Delta H_{\text{ash}} &= \int_{25}^{1450} n_{\text{ash}} \cdot C_{p,\text{ash}} \cdot dT \\
&= n_i [(Cp, \text{ash}T)_{T=1450} - (Cp, \text{ash}T)_{T=242.6}] \\
&= 1.19 \cdot 10^5 (\text{mol/hr}) \cdot (72.99 (\text{kJ/mol}) - 12.63 (\text{kJ/mol})) \\
&= 7.17 \cdot 10^6 (\text{kJ/hr})
\end{aligned} \tag{3.6.7.7}$$

Finding the Total Energy Requirement:

$$\begin{aligned}
E &= \Sigma \Delta H_{\text{components}} + \Delta H_{\text{vap}} + n \cdot \Sigma \Delta H_{\text{reactions}} \\
&= (3.26 \cdot 10^8 + 6.01 \cdot 10^7 + 4.23 \cdot 10^7 + 1.32 \cdot 10^8 + 9.33 \cdot 10^7 + 7.17 \cdot 10^6 \\
&\quad + 8.14 \cdot 10^7 + (3.42 \cdot 10^5 \cdot 92.8) + (9.81 \cdot 10^4 \cdot 2430) + (9.53 \cdot 10^5 \cdot 230.5)) \text{ kJ/hr} \\
&= 1.23 \cdot 10^9 \text{ kJ/hr} \\
&= 342 \text{ MW}
\end{aligned} \tag{3.6.7.8}$$

Total Energy Requirement = 342 MW

4 Process Description and Simulation

4.1 ASPEN Plus Simulation

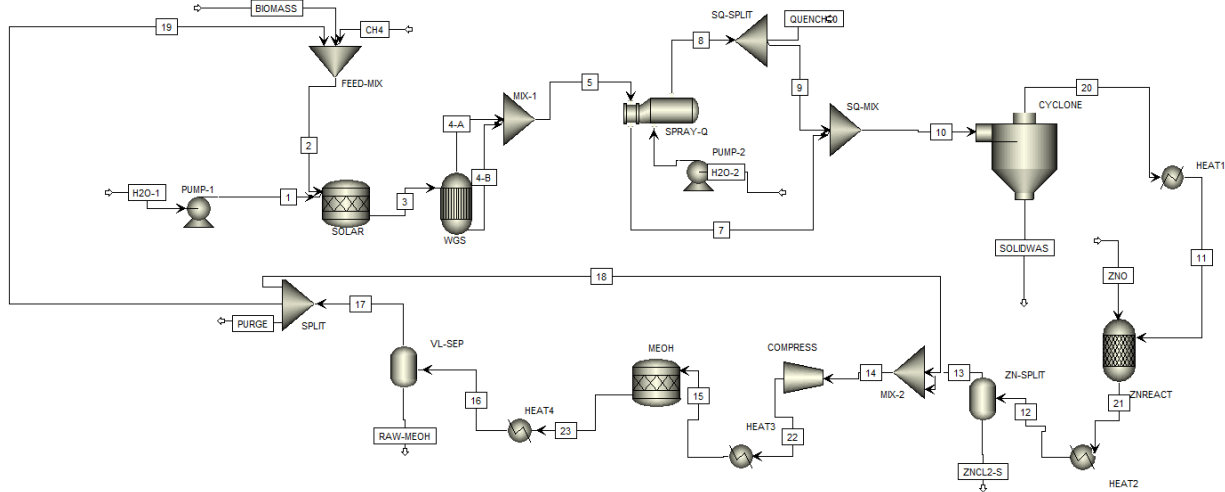


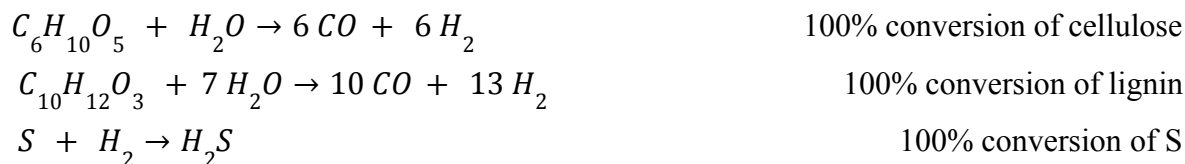
Figure 4.1.1 Aspen Simulation Model of the Overall Production Process

A summary of the key units in the Aspen Plus simulation was given. The completed, converged Aspen Plus simulation can be referenced in Appendix C.

4.1.1 Solar Thermal Reactor Unit

The biomass (BIOMASS) feed was mixed with the methane (CH4) feed and the recycle stream (19) from the end of the raw methanol production unit (SPLIT) before entering the solar reactor model (SOLAR). The first water stream (H2O-1) was also designed to be pumped up through the

first pump (PUMP-1) into the same solar reactor. The solar reactor itself was modeled by splitting it into two reactors, one of which would handle the reactions that went to completion while the other, the WGS unit (WGS), would handle the reversible reaction. The reactions for the solar reactor are as follows with respective conversions:



And the following reactions were performed in the equilibrium reactor:



The two streams from the WGS unit were mixed (MIX-1) and sent to the spray quench unit (SPRAY-Q) for cooling.

Table 4.1.1.1 Solar Thermal Reactor Unit Equipment Specification

Equipment	Temperature °C	Pressure (bar)	Heat Duty (J/s)	Pressure Difference (bar)
PUMP-1	—	—	—	+34
SOLAR	1450	35	—	—
WGS	800	35	—	—

Table 4.1.1.2 Solar Thermal Reactor Units Stream Specifications

Stream	Temperature °C	Pressure (bar)	Flow Rate (kmol/hr)	Composition (mol fractions)
BIOMASS	25	35	192.73	0.586 - Cellulose 0.168 - Lignin 0.203 - Ash 0.0004 - Sulfur 0.012 - Chlorine 0.03 - Nitrogen
CH4	25	35	848.1	1 - Methane
2	-36.11	35	1521	0.074 - Cellulose

				0.021 - Lignin 0.026 - Ash 1.8e-5 - Water 0.136 - Carbon Monoxide 0.152 - Hydrogen 5.42e-5 - Sulfur 0.001 - Chlorine 0.557 - Methane 2.37e-6 - Carbon Dioxide 0.005 - Methanol 0.026 - Nitrogen
H2O-1	25	1	1188	1- Water
1	25.8	35	1188	1 - Water
3	1450	35	6021	0.006 - Ash 4.73e-5 - Water 0.342- Carbon Monoxide 0.643 - Hydrogen 1.37e-5 - Hydrogen Sulfide 0.0007 - Hydrogen Chloride 5.99e-7 - Carbon Dioxide 0.001 - Methanol 0.006 - Nitrogen
4A	800	35	5982	3.049e-5 - Water 0.344 - Carbon Monoxide 0.647 - Hydrogen 1.37e-5 - Hydrogen Sulfide 0.0008 - Hydrogen Chloride 1.77e-5 - Carbon Dioxide 0.001 - Methanol 0.007 - Nitrogen
4B	800	35	39.2	1 - Ash
5	800	35	6021	0.0065 - Ash 3.03e-5 - Water 0.341 - Carbon Monoxide 0.643- Hydrogen 1.37e-5 - Hydrogen Sulfide 7.5e-4 - Hydrogen Chloride 1.76e-5 - Carbon Dioxide 1.2e-4 - Methanol 6.6e-3 - Nitrogen

4.1.2 Spray Quench Unit

Syngas from the previous solar thermal reaction unit entered the spray quench unit where it was sprayed with water (H₂O-2) provided by the second pump (PUMP-2). While modeling this stage on ASPEN, the water flow rate through the spray quench had to be specified so sufficient cooling to the specified temperature of 210 °C (stream 10) was performed. Stream 10 was a combination of the purified heat exchanger steam (9) from the post spray-quench splitter (SQ-SPLIT) and the cooled material from the heat exchanger (7). To find the value of the water required for adequate cooling in this heat exchanger, a heat exchanger was simulated in ASPEN to find the heat that would be needed to achieve the outlet temperature. The outletting stream (10) from the mixer (SQ-MIX) was sent to a cyclone unit (CYCLONE) so that the stream could be purified and the solid waste extracted (SOLIDWAS). The resulting process stream (20) was then sent to the Zinc Oxide Reactor Unit.

Table 4.1.2.1 Spray Quench Unit Equipment Specifications

Equipment	Min. Temperature Approach °C	Pressure Difference (bar)	Split Fraction	Separation Sharpness	Offset of Fines
SPRAY-Q	0.5	–	–	–	–
PUMP-2	–	+34	–	–	–
SQ-SPLIT	–	–	0.005	–	–
CYCLONE	–	–	–	1	0.99

Table 4.1.2.2 Spray Quench Unit Stream Specifications

Stream	Temperature °C	Pressure (bar)	Flow Rate (kmol/hr)	Composition (mol fractions)
H ₂ O-2	25	1	3234	1 - WATER
7	212	35	6021	6.5e-4 - Ash 3.03e-5 - Water 0.341 - Carbon Monoxide 0.643- Hydrogen 1.37e-5 - Hydrogen Sulfide 7.5e-4 - Hydrogen Chloride 1.76e-5 - Carbon Dioxide 1.2e-3 - Methanol 6.6e-3 - Nitrogen

8	242.57	35	3234	1 - Water
9	242.56	35	16.17	1 - Water
QUENCH2O	242.56	35	3217.83	1 - Water
10	210.46	35	6037.5	6.5e-4 - Ash 3.03e-5 - Water 0.341 - Carbon Monoxide 0.643- Hydrogen 1.37e-5 - Hydrogen Sulfide 7.5e-4 - Hydrogen Chloride 1.76e-5 - Carbon Dioxide 1.2e-3 - Methanol 6.6e-3 - Nitrogen
20	210	35	5998	2.27e-5 - Water 0.343 - Carbon Monoxide 0.645 - Hydrogen 1.37e-5 - Hydrogen Sulfide 7.5e-4 - Hydrogen Chloride 1.77e-5 - Carbon Dioxide 1.2e-3 - Methanol 6.7e-3 - Nitrogen
SOLIDWAS	210	35	39.2	1- ASH

4.1.3 Zinc Oxide Reactor Unit

The gas stream (20) from the cyclone needed to be heated significantly to the desired inlet temperature of the upcoming zinc oxide reactor (ZNREACT) and so a heat exchanger (HEAT2) was implemented to heat this stream to 650°C. The resulting stream (11) was directed into the gas cleaning reactor to remove hydrogen sulfide and produce zinc sulfide by reaction with zinc oxide. The following reactions take place in this reactor:



The resulting mixture (21) was then cooled back down to the specified temperature (210 °C) using a heat exchanger (HEAT3). This cooled stream (12) was then sent to a flash separator (ZN-SPLIT) to remove the zinc chloride and zinc sulfide (ZNCI2-S). The resulting gas stream (13) was directed to the Raw Methanol Production Unit.

Table 4.1.3.1. Zinc Oxide Reactor Unit Equipment Specifications

Equipment	Temperature °C	Pressure (bar)	Heat Duty (J/s)
HEAT-1	–	–	2.13e7
ZN-REACT	650	35	–
HEAT-2	–	–	-2.29e7
ZN-SPLIT	650	35	–

Table 4.1.3.2 Zinc Oxide Reactor Unit Stream Specifications

Stream	Temperature °C	Pressure (bar)	Flow Rate (kmol/hr)	Composition (mol fractions)
11	650	35	5998	2.27e-5 - Water 0.343 - Carbon Monoxide 0.645 - Hydrogen 1.37e-5 - Hydrogen Sulfide 7.5e-4 - Hydrogen Chloride 1.77e-5 - Carbon Dioxide 1.2e-3 - Methanol 6.7e-3 - Nitrogen
ZNO	650	35	2.3529	1 - Zinc Oxide
21	650	35	5998	0.003 - Water 0.343 - Carbon Monoxide 0.646 - Hydrogen 1.77e-5 - Carbon Dioxide 1.37e-5 - Zinc Sulfide 3.8e-4 -Zinc Chloride 1.2e-3 - Methanol 6.7e-3 - Nitrogen
12	270	35	5998	0.003 - Water 0.343 - Carbon Monoxide 0.646 - Hydrogen 1.77e-5 - Carbon Dioxide 1.37e-5 - Zinc Sulfide 3.8e-4 -Zinc Chloride 1.2e-3 - Methanol 6.7e-3 - Nitrogen
ZNCI2-S	210	35	2.3529	0.035 - Zinc Sulfide 0.965 - Zinc Chloride

13	210	35	5995	0.003 - Water 0.343 - Carbon Monoxide 0.646 - Hydrogen 1.77e-5 - Carbon Dioxide 1.2e-3 - Methanol 6.7e-3 - Nitrogen
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4.1.4 Raw Methanol Production Unit

The process stream from the previous unit was mixed (MIX-2) with a recycle stream (18) in preparation for the methanol reaction. The resulting stream (14) was then compressed (COMPRESS) to 80 bars according to the pressure specification given in the problem statement. The pressurized stream (22) was sent to a heat exchanger (HEAT4) to be cooled from 290 °C to 270 °C in preparation for the reactor. The resulting stream (15) from this heat exchanger was fed to the methanol reactor (MEOH) and the following reactions with respective conversions were carried out:



The resulting reactor stream (22) was then sent to an additional heat exchanger (HEAT5) to be cooled from 420 °C to 270 °C. The material subjected to the reactor rose substantially in temperature because the reactions above were highly exothermic. The stream (16) coming out of the heat exchanger was sent to a separator (VL-Sep) to extract any methanol. This separation was not pure as other components were present with the methanol (see Table 4.1.4.2). This stream was sent to the downstream distillation unit described in the next section. The counter-stream (17) out of the separator was sent to a purge splitter (SPLIT) which produced three streams. The purge stream (PURGE) contained 0.5%wt of the inlet stream and was simply disposed of. The recycle stream fed back into the process with the feed biomass (19) contained 9.5%wt of the inlet stream. Stream 18, the methanol unit recycle steam, contained 90%wt of the inlet stream (17). This stream was recycled back to the beginning of the methanol process to be combined with stream 13.

Table 4.1.4.1 Raw Methanol Production Unit Equipment Specifications

Equipment	Temperature °C	Pressure (bar)	Heat Duty (J/s)	Pressure Change (bar)	Split Fractions
COMPRESS	–	–	–	+45	–

HEAT3	–	–	-1.38e7	–	–
MEOH	420	80	–	–	–
HEAT4	–	–	-1.96e7	–	–
VL-Sep	50	30	–	–	–
SPLIT	–	–	–	–	0.005 - PURGE 0.095 - 19 0.90 - 18

Table 4.1.4.2 Raw Methanol Production Unit Stream Specifications

Stream	Temperature °C	Pressure (bar)	Flow Rate (kmol/hr)	Composition (mol fractions)
14	140.8	35	10554	1.79e-3 - Water 0.381- Carbon Monoxide 0.574- Hydrogen 1.33e-5- Carbon Dioxide 7.3e-3 - Methanol 0.035 - Nitrogen
22	290.54	80	10554	1.79e-3 - Water 0.381- Carbon Monoxide 0.574- Hydrogen 1.33e-5- Carbon Dioxide 7.3e-3 - Methanol 0.035 - Nitrogen
15	270	80	10554	1.79e-3 - Water 0.381- Carbon Monoxide 0.574- Hydrogen 1.33e-5- Carbon Dioxide 7.3e-3 - Methanol 0.035 - Nitrogen
23	420	80	6929	2.75e-3 - Water 0.319 - Carbon Monoxide 0.352 - Hydrogen 6.13e-6 - Carbon Dioxide 0.273 - Methanol 0.053 - Nitrogen
16	270	80	6929	2.75e-3 - Water 0.319 - Carbon Monoxide

				0.352 - Hydrogen 6.13e-6 - Carbon Dioxide 0.273 - Methanol 0.053 - Nitrogen
RAW-MeOH	50	35	1864	0.010 - Water 0.014 - Carbon Monoxide 1.7e-3 - Hydrogen 2.4e-6 - Carbon Dioxide 0.972 - Methanol 2.2e-3 - Nitrogen
17	50	35	5064	5.73e-5 - Water 0.433- Carbon Monoxide 0.481- Hydrogen 7.5e-6- Carbon Dioxide 0.015- Methanol 0.072 - Nitrogen
PURGE	50	35	25.3	5.73e-5 - Water 0.433- Carbon Monoxide 0.481- Hydrogen 7.5e-6- Carbon Dioxide 0.015- Methanol 0.072 - Nitrogen
19	50	35	481	5.73e-5 - Water 0.433- Carbon Monoxide 0.481- Hydrogen 7.5e-6- Carbon Dioxide 0.015- Methanol 0.072 - Nitrogen
18	50	35	4558	5.73e-5 - Water 0.433- Carbon Monoxide 0.481- Hydrogen 7.5e-6- Carbon Dioxide 0.015- Methanol 0.072 - Nitrogen

4.2 ASPEN HYSYS Simulation

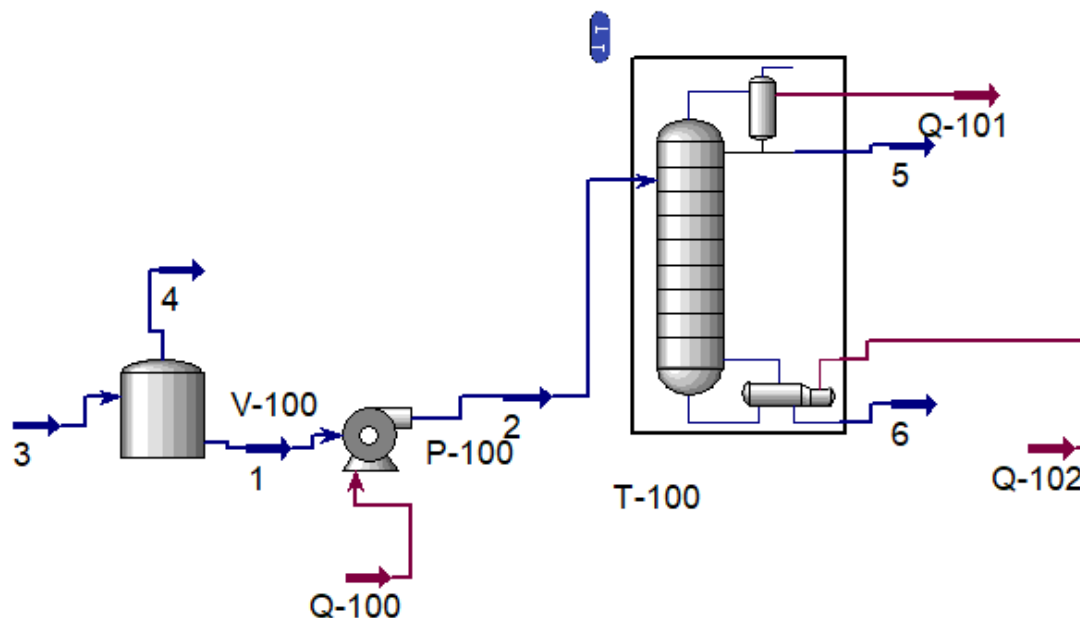


Figure 4.2.1 Aspen Simulation for the Downstream Process

The product stream was then used to determine the feed stream of the HYSYS simulation (3). The compositions were the same for the two streams, however the molar flow rate was changed due to the downstream methanol purification process being run for 8000 hours a year while the processes modeled in Aspen were run for 2920 hours a year. The inlet stream was directed into a storage tank where contaminant vapors were evolved off into vapor stream (4). The liquid stream from the storage tank (1) then entered pump P-100 at 1.013 bar and exited as stream (2) at 2.068 bar which was pumped to the separator where it was split into distillate stream (5) and bottoms stream (6). The product, distillate stream (5), was set to be 0.9997% methanol.

Table 4.2.1 Downstream HYSYS Stream Specifications

Stream	Temperature °C	Pressure (bar)	Flow Rate (kmol/hr)	Composition (mol fractions)
3	20	1.013	675.8	0.010 - Water 0.014 - Carbon Monoxide 1.7e-3 - Hydrogen 2.4e-6 - Carbon Dioxide 0.972 - Methanol 2.2e-3 - Nitrogen
4	20	1.013	13.61	0.0005 - Water

				0.6796 - Carbon Monoxide 0.0855 - Hydrogen 0.0001 - Carbon Dioxide 0.1271 - Methanol 0.1073 - Nitrogen
1	20	1.013	662.2	0.0103 - Water 0.0002 - Carbon Monoxide 0.9895 - Methanol
2	20.05	2.068	662.2	0.0103 - Water 0.0002 - Carbon Monoxide 0.9895 - Methanol
5	70.84	2.068	560.7	0.0003 - Carbon Monoxide 0.9997 - Methanol
6	77.96	1.624	101.5	0.0669 - Water 0.9331 - Methanol

The distillation column at the end was also designed such that it converged with no errors as seen in figure 4.2.2 below. The tray spacing was found to be 0.7010m as any less was causing an error in the internals.

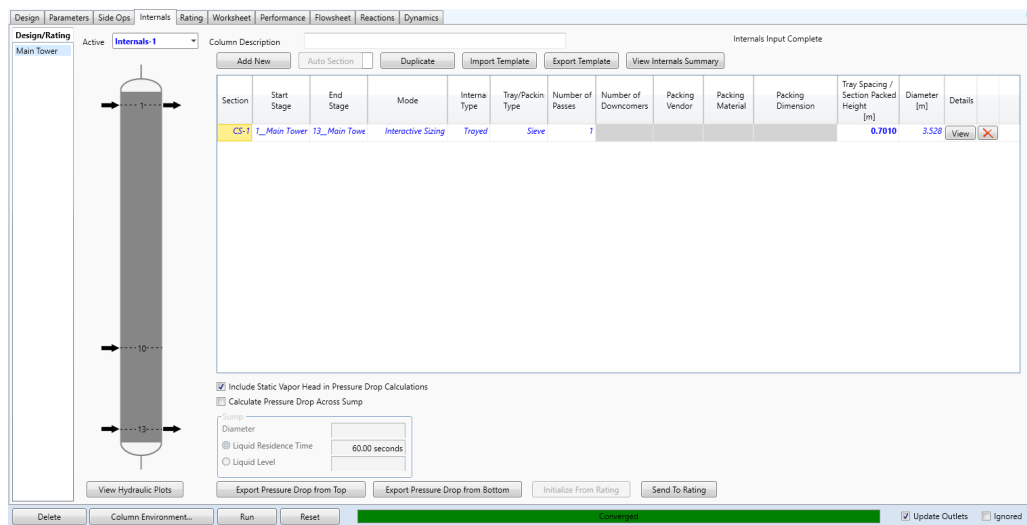


Figure 4.2.2 Distillation Column Convergence

The volumetric flow of the product stream was found to be 24.41 m³/hr, or 56.49 million gallons per year. The completed HYSYS file can be found in Appendix D.

5 Process Details and Equipment Specifications

5.1 Reactors

5.1.1 Solar Thermal Gasification Reactor

Process Role

The solar thermal reactor primarily did the work of converting waste biomass into syngas through a gasification reaction. This reactor was critical to the design of the process system, as much of the process is devoted to purifying the syngas produced in the solar thermal reactor and later converting it to raw methanol. Water, methane, and biomass at room temperature (25 °C) and 35 bar were fed into the reactor, along with trace amounts of several other chemical species due to the overall process recycle stream. Carbon monoxide and hydrogen gas were the primary products, though some byproducts such as hydrogen sulfide and hydrogen chloride were also produced. In essence, the solar thermal reactor could be thought of as providing the reagents necessary for methanol production. Due to the very high temperature required, the solar thermal reactor was powered by concentrated sunlight from a series of heliostat fields.

Model Approach & Equation Development

Within the solar thermal reactor, five independent reactions took place. Cellulose and lignin from the biomass was reacted with water to create the carbon monoxide and hydrogen gas syngas products. Methane, which was fed separately as a reactive sweep gas, also reacted with water to form syngas. Two side reactions also occurred, with sulfur and chlorine present in the biomass reacting with hydrogen gas in order to form the waste byproducts of hydrogen sulfide and hydrogen chloride. The stoichiometric reactions are listed below, as follows:



Reactions 1, 2, and 5 as labeled above could be described by a simplified reaction:



For the purposes of modeling this reactor, this simplified form of the reaction was substituted for the specific reactions of cellulose, methane, and lignin into syngas. In order to make this substitution, the decomposition of cellulose, lignin, and methane had to be taken into account. It was assumed that decomposition took place instantaneously upon the biomass entering the reactor, and accordingly the inlet flow rates of water and hydrogen gas were adjusted to account for the additional amount of each species that would be formed during the decomposition. The decomposition reactions are provided below:



Since the decomposition reactions were assumed to be instantaneous, no rate of decomposition was required. Additionally, the heats of decomposition were neglected from the energy balances, which will be described in depth later on. The assumption that the three syngas forming reactions could be described by one common form vastly simplified the species mass balances and reaction rates that were required to describe the system. Further simplification could also be accomplished by neglecting the side reactions of sulfur and chloride gas that occurred within the reactor. The reaction of interest was exclusively the conversion of biomass carbon into syngas carbon monoxide and hydrogen gas, and accordingly while it would be reasonable to assume that the conversions of sulfur into hydrogen sulfide and chlorine into hydrogen chloride were occurring simultaneously, they were neglected as inconsequential to the design of the solar thermal reactor. Finally, the water-gas shift (5.1.1.10) was assumed to occur instantaneously upon the process stream exiting the solar thermal reactor, and so the kinetics were neglected.



Therefore, the only relevant rate of reaction was that for reaction 5.1.1.6. Based upon the reaction kinetics (5.1.1.11) determined by Woodruff et. al., the material balance was derived^[5.1.1.14].

$$r = \frac{dX}{dt} = k_o(1 - X)\sqrt{1 - \phi * \ln(1 - X)} \quad (5.1.1.11)$$

To maintain consistent units, it was preferable to put the rate law in terms of molar flow rate rather than conversion. Additionally, the integration was to be performed along the length of the reactor rather than with respect to time. To perform these conversions, the definition of

conversion was applied, as well as a chain rule conversion of the derivative to get the rate with respect to length of the reactor.

$$\frac{dF_c}{dz} = \left(\frac{dX}{dt}\right)\left(\frac{dF_c}{dX}\right)\left(\frac{dt}{dz}\right) \quad (5.1.1.12)$$

$$F_i = F_{i0}(1 - X) \quad (5.1.1.13)$$

Rearranging this formula gave an expression for the (1-X) term given in the rate equation.

$$(1 - X) = \frac{F_i}{F_{i0}} \quad (5.1.1.14)$$

$$\frac{dF_c}{dX} = F_{c0} \quad (5.1.1.15)$$

$$\frac{dt}{dz} = (v_g)^{-1} \quad (5.1.1.16)$$

Accordingly, with carbon as the species of interest, the rate equation could be re-expressed as given by equation 5.1.1.17 with units of moles per meter-hour.

$$r_c = \frac{dF_c}{dz} = F_{c0} * \frac{k_0}{v_g} * \frac{F_c}{F_{c0}} * \sqrt{1 - \varphi * \ln\left(\frac{F_c}{F_{c0}}\right)} \quad (5.1.1.17a)$$

$$r_c = \frac{dF_c}{dz} = \frac{k_0}{v_g} * F_c * \sqrt{1 - \varphi * \ln\left(\frac{F_c}{F_{c0}}\right)} \quad (5.1.1.17b)$$

Equation 5.1.1.18 gives the expression for the kinetic constant k_0 , and the kinetic constant parameters have been provided in Table 5.1.1.1.

$$k_0 = \frac{K_1 p_{H_2O}}{1 + K_2 p_{H_2O} + K_3 p_{H_2}} \quad (5.1.1.18)$$

$$K_1 = k_1 \exp(-E_1/RT) \quad (5.1.1.19)$$

$$K_2 = k_2 \exp(-E_2/RT) \quad (5.1.1.20)$$

$$K_3 = k_3 \exp(-E_3/RT) \quad (5.1.1.21)$$

Table 5.1.1.1. Kinetic Parameters for Carbon Gasification (Woodruff et. al.)^[5.1.1.14]

Parameter	Unit	Value
k_1	$\text{bar}^{-1} \cdot \text{s}^{-1}$	$2.51 \cdot 10^3$
k_2	bar^{-1}	$6.74 \cdot 10^{-2}$
k_3	bar^{-1}	$3.04 \cdot 10^{-1}$
E_1	kJ/mol	112.6
E_2	kJ/mol	-37.3
E_3	kJ/mol	-36.6
φ	Unitless	4.3

The solar thermal reactor could be depicted as a vertical transport tube filled with downward flowing gas and solid particles. It was assumed that there was no significant pressure drop, and that the pressure in the reactor remained constant at 35 bar.

Two separate energy balances were required to model the temperature along the length of the reactor. Due to the high reactor temperature, the majority of the chemical species present were in the gas phase. However, carbon flowed through the reactor as particles, and therefore was subject to radiative (in addition to convective) heat transfer. One energy balance was required for the gas-phase species, and another for the particulate species. Including the non-reactive species, the gas phase consisted of sulfur, hydrogen sulfide, chlorine, hydrochloric acid, methanol, carbon monoxide, steam, carbon dioxide, and hydrogen gasses. The particulate species were ash and carbon. It was assumed that the temperature of the wall of the reactor was kept constant at 1450 °C.

The particle energy balance was derived based upon the equations provided by Dahl et. al.^[5.1.1.2]. The form of the equation as given by the Dahl et. al. paper is provided as equation 5.1.1.22. The paper described energy balances in a vertical reactor with a decomposition of methane occurring. The first term described the effects of the heat of reaction. The second term referred to convective heat transfer from the particles to the gas surrounding them. The third term expressed the radiative heat transfer from the walls to the particles.

$$\frac{dT_c}{dz} = \frac{-F_{CH_4}^0 * H_c(T_c)}{F_c C_{pc}} \frac{dX}{dz} - \frac{h_p a_c A_i n_c (T_c - T_g)}{F_c C_{pc}} + \frac{\varepsilon_c \sigma a_c A_i n_c (T_w^4 - T_c^4)}{F_c C_{pc}} \quad (5.1.1.22)$$

In the solar thermal reactor, there were both carbon and ash particles present. It was assumed that the ash particles were generally identical to the carbon particles with the exception of their weight and heat capacity. The heat of reaction was assumed to be constant at the reaction temperature rather than utilizing an equation for the enthalpy of the component species as a function of temperature. The modified form of the particle energy balance equation is provided below.

$$\frac{dT_c}{dz} = \frac{\Delta H_{rxn}^* r_c}{(F_c C_{pc} + F_{Ash} C_{pAsh})} - \frac{h_p a_c A_i n_c (T_c - T_g)}{(F_c C_{pc} + F_{Ash} C_{pAsh})} + \frac{\varepsilon_c \sigma a_c A_i n_c (T_w^4 - T_c^4)}{(F_c C_{pc} + F_{Ash} C_{pAsh})} \quad (5.1.1.23)$$

$$n_c = \frac{(F_c MW_c + F_{Ash} MW_{Ash})}{v_g A_i V_c \rho_c} \quad (5.1.1.24)$$

$$h_p = k_g / R_0 \quad (5.1.1.25)$$

The calculation of the heats of reaction and heat capacities are provided in the following section. The remainder of the variables and their values are summarized in Table 5.1.1.2.

Table 5.1.1.2 Particle Energy Balance Constants

Variable	Description	Value	Units	Source
MW_c	Molecular weight of carbon	12.01	g/mol	--
MW_{Ash}	Molecular weight of ash	60.086	g/mol	Problem statement
a_c	Surface area of carbon particles	$3.1 * 10^{-8}$	m ²	[5.1.1.2]
A_i	Cross sectional area of the reactor	--	m ²	Arbitrary
ε_c	Radiative emissivity of carbon	1	Unitless	[5.1.1.2]
σ	Stefan-Boltzmann constant	$5.76 * 10^{-8}$	W/m ² -K ⁴	--
v_g	Velocity of the gas phase	--	m/s	Arbitrary

V_c	Volume of carbon particle	$5.2 * 10^{-13}$	m^2	[5.1.1.2]
ρ_c	Density of carbon	2270	kg/m^3	[5.1.1.2]
k_g	Thermal conductivity of methane at 1450 C	0.26119	W/m-K	[5.1.1.4]
R_0	Carbon particle radius	$5 * 10^{-5}$	m	[5.1.1.2]
T_w	Wall temperature	1450	$^{\circ}C$	Problem statement

The energy balance for the gas phase reaction was similarly derived. The expression drawn from the Dahl et. al. paper is expressed in its original form in equation 5.1.1.26, with h_p defined as in equation 5.1.1.25^[5.1.1.2]. The first term again referred to the effects of the heats of reaction on the temperature of the gas. The second term was specific to the reactor design modeled by Dahl et. al, where hydrogen was introduced through the reactor wall along the length of the reactor. This term was therefore neglected from the energy balance for the solar thermal reactor. The third term described the convective heat transfer between the gas and the wall of the reactor, and the fourth and final term referred to convective heat transfer between the particles and the gas phase. The gas phase for the solar thermal reactor consisted of many different chemical species, specifically sulfur, hydrogen sulfide, chlorine, hydrochloric acid, methanol, carbon monoxide, steam, carbon dioxide, and hydrogen gasses.

$$\frac{dT_g}{dz} = \frac{F_{CH_4}^0 [H_{CH_4}(T_g) - 2H_{H_2}(T_g)] \frac{dX}{dz} + g \int_{T_g}^{T_w} C_{pH_2} dT + h_w \pi d_i (T_w - T_g) + h_p \frac{a F_c MW_c}{v_g V_g \rho_c} (T_c - T_g)}{F_{CH_4} C_{pCH_4} + F_{H_2} C_{pH_2}} \quad (5.1.1.26)$$

As before, the equation was expanded to account for all of the species present. In the particle phase both ash and carbon were included as in the particle energy balance, and the denominator of the reactor, therefore, summed the products of heat capacity and flow rate for each of those species. The final simplified form of this reaction was given in equation 5.1.1.27, with the convective heat transfer coefficient h_w given as in equation 5.1.1.28 and the variables not provided in Table 5.1.1.2 included below in Table 5.1.1.3. It was assumed that the film temperature, T_f , was equal to the wall temperature. Heat capacities and heats of reactions will be covered in more depth in subsequent sections. For equations 5.1.1.29-30, the summations of species i only refer to the gas phase species.

$$\frac{dT_g}{dz} = \frac{(\Delta H_{rxn} * r_c) + h_w \pi D (T_w - T_g) + h_p \frac{a(F_c MW_c + F_{Ash} MW_{Ash})}{v_g V_c \rho_c} (T_c - T_g)}{F_S C_{pS} + F_{H_2S} C_{pH_2S} + F_{Cl_2} C_{pCl_2} + F_{HCl} C_{pHCl} + F_{MeOH} C_{pMeOH} + F_{CO} C_{pCO} + F_{H_2O} C_{pH_2O} + F_{CO_2} C_{pCO_2} + F_{H_2} C_{pH_2}} \quad (5.1.1.27)$$

$$h_w = 0.034 * \left[\frac{k_g(T_f)}{D} \right] * \left[\frac{F_g MW_g D}{A_i \mu (T_f)} \right]^{0.8} * \left(\frac{T_g}{T_f} \right)^{0.8} * \left[\frac{C_{pg}(T_f) * \mu (T_f)}{k_g(T_f) MW_g} \right]^{0.4} * \left(\frac{L}{D} \right)^{0.1} \quad (5.1.1.28)$$

$$Cp_g = \frac{\sum_i F_i * C_{pi}}{\sum_i F_i} \quad (5.1.1.29)$$

$$MW_g = \frac{\sum_i F_i * MW_i}{\sum_i F_i} \quad (5.1.1.30)$$

Table 5.1.1.3 Gas Phase Energy Balance Constants

Variable	Description	Value	Units	Source
d_i	Inside diameter of reactor tube	0.076	m	[5.1.1.2]
μ_g	Viscosity of gas phase	0.04650	cP	[5.1.1.5]
T_f	Film temperature	1450	C	Assumption
L	Reactor length	--	m	Arbitrary

This concluded the necessary mass and energy balances to be implemented in MatLab, with the exception of the temperature dependent heat of reaction and heat capacity calculations to be performed as follows.

Heats of Reaction & Heat Capacity Calculations

Temperature dependent heat capacity formulas were found for all of the chemical compounds present in the reactor. The form of the heat capacity equation as a function of temperature was also determined to correspond with the heat capacity constants that were found for each chemical compound present. There were two species for which heat capacity as a function of temperature could not be found in the literature: the heat capacity of ash at 285 K was used as a constant, as was the heat capacity of methanol at the reactor temperature of 1723 K. For all other species, the heat capacity constants have been tabulated in Table 5.1.1.4.

Table 5.1.1.4 Heat Capacity Constants For the Solar Thermal Reactor

Species	A	B	C	D	E	Form	Source
CH_4	85.8127	11.26467	-2.114146	0.13819	-26.4221	2	[5.1.1.7]
C	21.1751	-0.812428	0.448537	-0.043256	-0.013103	2	[5.1.1.8]
H_2	$28.84 \cdot 10^{-3}$	$0.00765 \cdot 10^{-5}$	$0.3288 \cdot 10^{-8}$	$-0.8698 \cdot 10^{-12}$	--	1	[5.1.1.15]
$C_6H_{10}O_5$	-0.011704	0.0006721	--	--	--	1	Problem Statement
$C_{10}H_{12}O_3$	0.03143	0.0003994	--	--	--	1	Problem Statement
$H_2O(g)$	$33.46 \cdot 10^{-3}$	$0.688 \cdot 10^{-5}$	$0.7604 \cdot 10^{-8}$	$-3.593 \cdot 10^{-12}$	--	1	[5.1.1.15]
CO	$28.95 \cdot 10^{-3}$	$0.411 \cdot 10^{-5}$	$0.3548 \cdot 10^{-8}$	$-2.22 \cdot 10^{-12}$	--	1	[5.1.1.15]
S	-37.9335	133.242	-95.3245	24.0094	7.65453	2	[5.1.1.9]
H_2S	51.22136	4.147486	-0.643566	0.041621	-10.46385	2	[5.1.1.10]
Cl_2	$33.6 \cdot 10^{-3}$	$1.367 \cdot 10^{-5}$	$-1.607 \cdot 10^{-8}$	$6.743 \cdot 10^{-12}$	--	1	[5.1.1.15]
HCl	$29.13 \cdot 10^{-3}$	$-0.1341 \cdot 10^{-5}$	$0.9715 \cdot 10^{-8}$	$-4.335 \cdot 10^{-12}$	--	1	[5.1.1.15]
N_2	19.50583	19.88705	-8.598535	1.369784	0.527601	2	[5.1.1.11]
$MeOH$	109.68	--	--	--	--	3	[5.1.1.12]
CO_2	58.16639	2.720074	-0.492289	0.038844	-6.447293	2	[5.1.1.13]
Ash	42.36063	--	--	--	--	3	Problem Statement

The heat capacity equations for the various forms were provided in order to convert between the heat capacity constants and heat capacity as a function of temperature. Temperature for all forms was in Kelvins.

$$\text{Form 1: } C_p [kJ/mol - K] = (A + BT + CT^2 + DT^3) \quad (5.1.1.31)$$

$$\text{Form 2: } C_p [J/mol - K] = A + B\left(\frac{T}{1000}\right) + C\left(\frac{T}{1000}\right)^2 + D\left(\frac{T}{1000}\right)^3 + \frac{E}{\left(\frac{T}{1000}\right)^2} \quad (5.1.1.32)$$

$$\text{Form 3: } C_p [kJ/mol - K] = A \quad (5.1.1.33)$$

Due to the assumptions made earlier in establishing the material and energy balances, it was assumed that the only relevant reaction providing heat to the reactor was that described by equation 5.1.1.6, the conversion of carbon and steam to carbon monoxide and hydrogen syngas. The heat of reaction was therefore only calculated for this reaction. The products were defined to be hydrogen gas and carbon monoxide, and the reactants will refer to the water vapor and carbon particles.

It was assumed that the heat of reaction could be assumed to be constant at the reactor temperature, which was in turn assumed to be the wall temperature (1450 °C, or 1723 K). There were three parts to calculating the heat of reaction at this temperature. The reactants had to be reduced from the reactor temperature to the standard reference temperature of 298 K. Heats of formation at the reference temperature were used to calculate the heat of reaction at 298 K. The products then had to be returned to the reactor temperature. Due to enthalpy being a state function, this series of steps gave an overall change in enthalpy equal to that which would be obtained by reacting at 1723 K. These steps could be summarized with the following equations, with “n” as the coefficient of the compound in the chemical reaction. The heats of formation have been recorded in Table 5.1.1.5.

$$\Delta H_{rxn, 1743 K} = \sum_1^3 \Delta H_n \quad (5.1.1.34)$$

$$\Delta H_1 = \int_{1723 K}^{298 K} \sum_{\text{Reactants}} n c_p dT \quad (5.1.1.35)$$

$$\Delta H_2 = \sum n \Delta H_{f, products}^0 - \sum n \Delta H_{f, reactants}^0 \quad (5.1.1.36)$$

$$\Delta H_3 = \int_{298 K}^{1723 K} \sum_{\text{Products}} n c_p dT \quad (5.1.1.37)$$

Table 5.1.1.5 Heats of Formation for the Solar Thermal Reactor

Species	Coefficient (n)	ΔH_f^o (kJ/mol)	Source
C	1	0	[5.1.1.1]
H ₂ O	1	-241.82	[5.1.1.3]
CO	1	-110.53	[5.1.1.3]
H ₂	1	0	[5.1.1.3]

In the calculation of ΔH_1 as expressed by equation 5.1.1.35, the form of the equation could be expanded to specify the precise variables involved and then simplified in order to allow for the calculation to be performed.

$$\Delta H_1 = n_C \int_{1723 K}^{298 K} c_{pC} dT + n_{H_2O} \int_{1723 K}^{298 K} c_{pH_2O} dT \quad (5.1.1.38)$$

$$\begin{aligned} \Delta H_1 = n_C \int_{1723 K}^{298 K} [A + B(\frac{T}{1000}) + C(\frac{T}{1000})^2 + D(\frac{T}{1000})^3 + \frac{E}{(\frac{T}{1000})^2}] dT \\ + n_{H_2O} \int_{1723 K}^{298 K} [A + BT + CT^2 + DT^3]_{H_2O} dT \end{aligned} \quad (5.1.1.39)$$

$$\begin{aligned} \Delta H_1 = n_C [A(\frac{T}{1000}) + \frac{B}{2}(\frac{T}{1000})^2 + \frac{C}{3}(\frac{T}{1000})^3 + \frac{D}{4}(\frac{T}{1000})^4 - \frac{E}{(\frac{T}{1000})}]_{298 K} \\ - n_C [A(\frac{T}{1000}) + \frac{B}{2}(\frac{T}{1000})^2 + \frac{C}{3}(\frac{T}{1000})^3 + \frac{D}{4}(\frac{T}{1000})^4 - \frac{E}{(\frac{T}{1000})}]_{1723 K} \\ + n_{H_2O} [AT + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4]_{298 K} - n_{H_2O} [AT + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4]_{1723 K} \end{aligned} \quad (5.1.1.40)$$

$$\Delta H_1 = - 62.61 \text{ kJ/mol} \quad (5.1.1.41)$$

The calculation of ΔH_3 was performed in a very similar manner.

$$\Delta H_3 = n_{CO} \int_{298 K}^{1723 K} c_{pCO} dT + n_{H_2} \int_{298 K}^{1723 K} c_{pH_2} dT$$

$$\Delta H_3 = n_C \int_{298 K}^{1723 K} [A + BT + CT^2 + DT^3]_{CO} dT + n_{H_2O} \int_{298 K}^{1723 K} [A + BT + CT^2 + DT^3]_{H_2} dT \quad (5.1.1.42)$$

$$\Delta H_3 = n_{CO} [AT + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4]_{1723 K} - n_C [AT + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4]_{298 K} + n_{H_2} [AT + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4]_{1723 K} - n_{H_2} [AT + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4]_{298 K} \quad (5.1.1.43)$$

$$\Delta H_1 = 93.17 \text{ kJ/mol} \quad (5.1.1.44)$$

The calculation of ΔH_2 was dependent on the heats of formation rather than the heat capacities and was accordingly easier to calculate since no integration was required. Using the values provided in Table 5.1.1.5, this term was calculated as shown below.

$$\Delta H_2 = n_{CO} \Delta H_{f,CO}^o + n_{H_2} \Delta H_{f,H_2}^o - n_C \Delta H_{f,C}^o - n_{H_2O} \Delta H_{f,H_2O}^o \quad (5.1.1.45)$$

$$\Delta H_2 = (1)(-110.53) + (1)(0) - (1)(0) - (1)(-241.82) = 131.29 \text{ kJ/mol} \quad (5.1.1.46)$$

The overall heat of reaction was calculated through summing the intermediate component changes in enthalpy for each of these three steps. Thus,

$$\Delta H_{rxn, 1723 K} = (-62.61) + (93.17) + (131.29) = 161.86 \text{ kJ/mol} \quad (5.1.1.47)$$

Complete Excel calculations of the heat of reaction are provided in Appendix E and can be referenced if more detail should be required. The heat capacity and heat of reaction values found in this section were used in the energy balances when appropriate, as explained in detail in the section on the development of equations, above.

Model Results & Discussion

There were two options for the design of the solar thermal reactor, based upon the solution to the simultaneous material and energy balances. Section 5.5, detailing the design of the heliostat towers and fields that supply energy to the solar thermal reactor, found that the most economically feasible option was to use two towers and their surrounding fields to supply the needed amount of energy to the reactor. Accordingly, there were two options for the reactor design: a single solar thermal reactor, which would need to have energy supplied from multiple towers, or two smaller solar thermal reactors directly connected to each tower. Each scenario was set up in MatLab, and the two designs were modeled. Length, cross-sectional area, and velocity of gas through the reactor were all treated as arbitrary values that could be adjusted to get the

desired conversion. While complete conversion of carbon would have been ideal, the increase in reactor length required for increase in total conversion at high conversions would have been too large to be reasonable physically or economically.

With two separate reactors, each attached to one of the heliostat field towers, a reactor length of 20 meters (with cross-sectional area of 0.25 m^2 and velocity of gas 0.25 m/s) resulted in a 96% conversion of carbon. With only one reactor and heat fed into it from the two fields, with identical gas flow rate and velocity to the first case, increasing the reactor length by only five meters (25 m total) obtained a comparable conversion of 97%. Accordingly, it was more economically advantageous to use only one reactor, and to determine the best way to direct energy from the two heliostat fields into heating it. This also allowed for fewer pumps and heat exchangers than would have been required if the solar thermal reactor setup had to be doubled to account for two reactors. The single reactor design was therefore utilized. The full MatLab code used in the reactor design, as well as plots of the behavior of all present and chemical species, can be referenced in Appendix F. A summary of important results has been provided here as well in Figures 5.1.1.1-3.

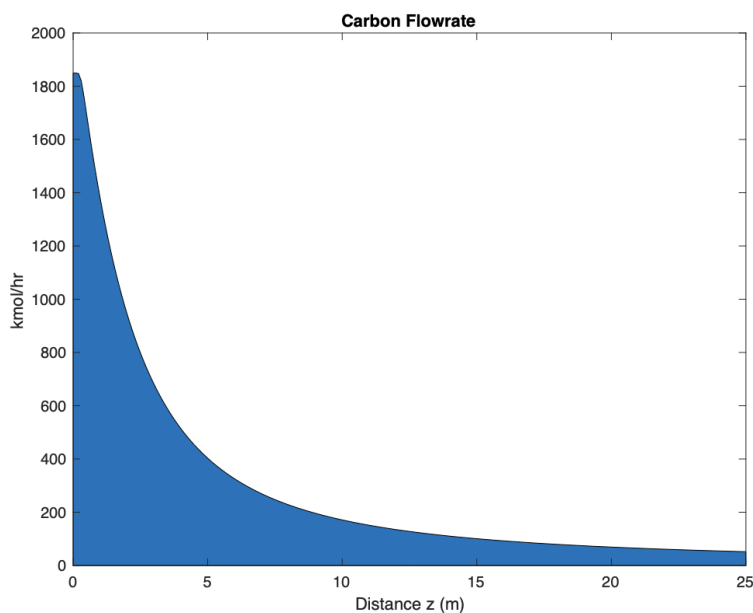


Figure 5.1.1.1 Flow rate of carbon along the length of the solar thermal reactor

Initially, the flowrate of carbon in the reactor remained essentially unchanged. This was due to the low temperature immediately entering the reactor. The entering particles and gas were both assumed to enter the reactor at room temperature, or 25°C (298 K). With a constant wall temperature of 1450°C (1723 K) and due to the small size of the particles and the low heat capacities of the gasses present, it did not take long for either the gas phase or the particles to reach temperatures near the wall temperature. Figures 5.1.1.2 and 5.1.1.3 revealed that the

temperature of both the particles and the gas increased dramatically within the first half a meter or so of entering the reactor. The behaviors of both phases were remarkably similar and had nearly the same temperature due to the heat exchanged between the phases and between the phases and the reactor wall. The high temperature in the reactor resulted in a high rate of conversion of carbon and steam to syngas, resulting in the approximately exponential decay of the carbon within the reactor.

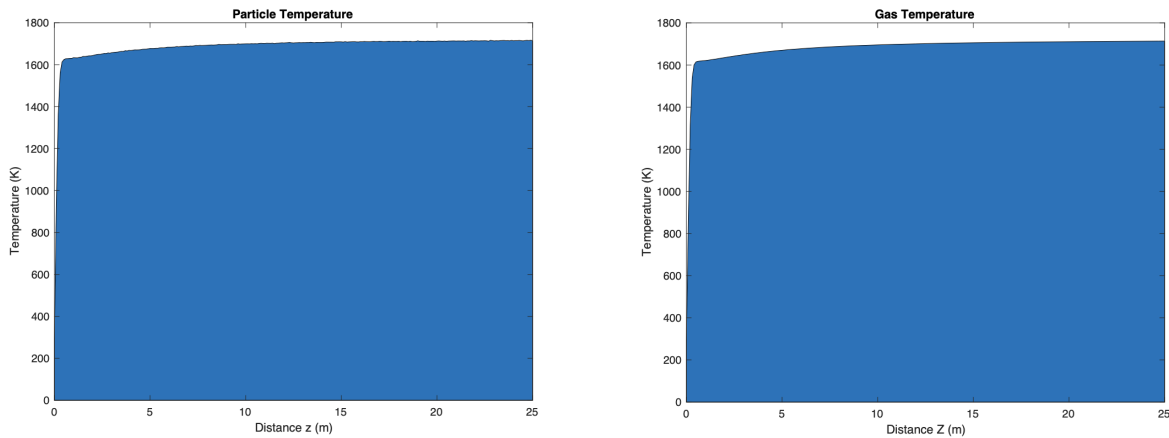


Figure 5.1.1.2 Particle temperature along the length of the solar thermal reactor

Figure 5.1.1.3 Gas phase temperature along the length of the solar thermal reactor

Description of Reactor

From the MatLab solution models, it was determined that one solar thermal reactor should be used with the energy supplied from two towers and their associated heliostat fields as described in section 5.5. The overall reactor length was 25 meters, giving a carbon conversion of approximately 97%. With a cross sectional area of 0.25 square meters and a generally cylindrical vertical reactor shape, the volume of the reactor was 6.25 cubic meters. While calculations were performed with an overall cross sectional area, the solar thermal reactor consisted of an overall reactor shell housing silicon carbide tubes. It was assumed that the presence of these tubes had no significant impact on the performance of the reactor compared to the model that was created neglecting them.

The silicon carbide tubes were listed as being twelve inches in outer diameter, with a thickness of $\frac{3}{4}$ of an inch. Converted to SI units, the inner cross sectional area would be approximately 0.06 square meters, and the outer cross sectional area would be approximately 0.07 square meters. Dividing the total cross sectional area of the larger reactor shell by the cross-sectional area taking into account the outer diameter of the silicon carbide tubes, 3.6 tubes could fit within. Assuming some amount of spacing in between the tubes, three silicon carbide tubes would be present within the solar thermal reactor. A stainless steel alloy (typically with chromium, nickel, and

molybdenum) should be used for this reactor design due to its ability to withstand high temperatures such as those experienced in this reactor^[5.1.1.6]. Figure 5.1.1.4 gives a basic sketch of the dimensions of this reactor as designed in this section of the report.

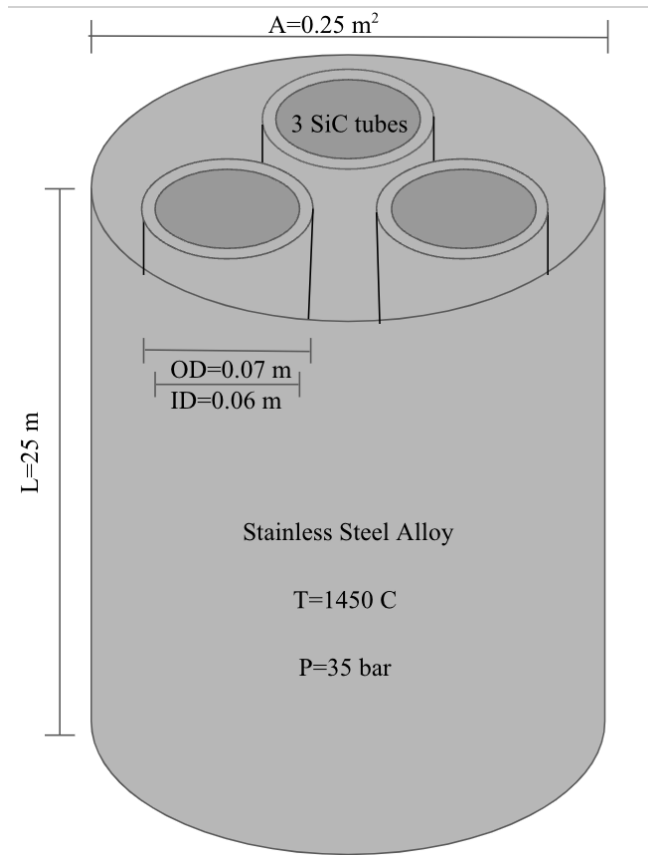


Figure 5.1.1.4 Visual representation of the solar thermal reactor

5.1.2 Catalytic Gas Cleaning Bed

Reactor Introduction

The zinc oxide bed reactor was used to convert solid zinc oxide to solid zinc chloride using hydrogen gas along with converting chlorine to gaseous hydrogen chloride as shown in the following reactions:



The reactor was modeled based on the following paper, written by Gibson et al, which follows a small-scale production process^[5.1.2.3]. This process would be scaled up to an industrial process with a reasonable amount of assumptions made. The main thing to know from this paper is that pellets were pretreated with zinc-oxide grains around the surface of the sphere. These grains

were 94.5% zinc oxide and resided on small (~0.18cm) pellets that flowed throughout a singular-tubed reactor. There was a small pressure drop to consider but the pressure drop was considered negligible since a solid and gas were flowing throughout the tubular reactor. The thermal behavior of the system was considered and the reactor was modeled as operating at much higher temperatures than suggested (650°C compared to 210°C) since residence times were found to be extremely long, requiring a very large reactor. Because of the higher temperature, an additional heat exchanger had to be implemented after the reactor to cool the extracted product back down to the specified temperature. Kinetics of the second hydrochloric acid reaction were neglected since literature was not available on the kinetics.

Heat of Reaction

The calculation process of this reaction was to first consider the heat of reaction produced or absorbed. This process was as follows:

$$\Delta H_{rxn} = \sum_{n=1}^3 \Delta H_n \quad (5.1.2.3)$$

For this expression,

$$\Delta H_1 = \int_{210}^{25} \sum n c_p dT \quad (5.1.2.4)$$

$$\Delta H_2 = \sum_i \Delta H_{f,products,i} - \sum_i \Delta H_{f,reactants,i} \quad (5.1.2.5)$$

$$\Delta H_3 = \int_{25}^{210} \sum n c_p dT \quad (5.1.2.6)$$

In finding the heat capacities of species involved in the reactions, the heat capacity values of the solids were assumed to be constant regardless of temperature because of the strict molecular activity involved in heating solids with very high melting points (ZnO, ZnS, and ZnCl₂ have melting points well above the discussed operating temperatures). The heat capacity values for the solids were as follows:

Table 5.1.2.1. Heat Capacity Values of Solid Species

Species	Heat Capacity (J/mol-°C)	Source
---------	--------------------------	--------

ZnO	0.0494	[5.1.2.8]
ZnS	0.469	[5.1.2.1]
ZnCl ₂	0.73954	[5.1.2.4]

Heat capacity values for gasses had to be integrated over temperature since their composite values were sensitive to temperature changes as per the principles of thermal expansion. The following table shows constants used for these integrations:

Table 5.1.2.2. Heat Capacity Values of Gaseous Species [5.1.2.2]

Species	A*10 ³	B*10 ⁵	C*10 ⁸	D*10 ¹²	Range(C)
H ₂ S(g)	33.51	1.547	0.3012	-3.292	0-1500
H ₂ O(g)	33.46	0.6680	0.7604	-3.593	0-1500
HCl(g)	29.13	-0.1341	0.9715	-4.335	0-1200

Using these constants, the following integrations were performed for the products and reactants of reaction 5.1.1.1.

Reactants:

$$\begin{aligned}
 \Delta H_1 &= \int_{210}^{25} n_{H_2S} c_{p,H_2S} dT + n_{ZnO} c_{p,ZnO} dT & (5.1.2.7) \\
 &= \int_{210}^{25} n_{H_2S} * (A_{H_2S} + B_{H_2S} T + C_{H_2S} T^2 + D_{H_2S} T^3) dT + n_{ZnO} c_{p,ZnO} dT \\
 &= n_{H_2S} \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25C, H_2S} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=210C, H_2S} \right] + \\
 &\quad n_{ZnO} c_{p,ZnO} dT \\
 &= -333 \text{ J/mol}
 \end{aligned}$$

Products:

$$\begin{aligned}
 \Delta H_3 &= \int_{25}^{210} n_{H_2O} c_{p,H_2O} dT + n_{ZnS} c_{p,ZnS} dT & (5.1.2.8) \\
 &= \int_{25}^{210} n_{H_2O} * (A_{H_2O} + B_{H_2O} T + C_{H_2O} T^2 + D_{H_2O} T^3) dT + n_{ZnS} c_{p,ZnS} dT \\
 &= n_{H_2O} \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=210C, H_2O} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=25C, H_2O} \right] +
 \end{aligned}$$

$$n_{ZnS} C_{p,ZnS} dT$$

$$= 316 \text{ J/mol}$$

The heat of formation values were taken as shown in the following table:

Table 5.1.2.3. Heat of Formations of Species in the Hydrochloric Acid Reaction

Species	Heat of Formation (kJ/mol)	Source
ZnO	-350,460	[5.1.2.5]
H ₂ S	-19,960	[5.1.2.2]
ZnS	-49,200	[5.1.2.6]
H ₂ O	-285,840	[5.1.2.2]

Using the heat of formation values listed above, the summed heat of formation for the reaction (5.1.1.1) was calculated as follows:

$$\Delta H_2 = \sum_i \Delta H_{f,products,i} - \sum_i \Delta H_{f,reactants,i} = 35380 \text{ J/mol} \quad (5.1.2.9)$$

To calculate the heat of reaction, the following sum of enthalpies was performed:

$$\Delta H_{rxn} = \sum_1^3 \Delta H_n = 35,363 \text{ J/mol} \quad (5.1.2.10)$$

This value was the amount of heat that the reaction consumed per mole of reactant that was consumed. This value was expected to be exothermic since this was an adsorption reaction but was surprisingly endothermic. Regardless, the reaction process was carried out as follows.

Design Considerations

In considering the phases of the species that reacted in this reactor (solid and gas), it was determined that a singular tubular reactor would be best used rather than a multi-tube reactor. This was mainly in consideration of the solid phases that would presumably have much lower mass transfer in a smaller volume, as would be the case for a multi-tube reactor of the same total reactor volume. Since a heat exchanger was used before this reactor, optimal heat transfer was not considered to get the reactants up to specified temperature. The only heat transfer that needed to be considered was the flow of heat transfer fluid that would be used to keep the reactor at the

reaction temperature. These considerations confirmed the idea that a singular tubular reactor should be used.

A constant-stirred tank reactor was also considered for usage but was quickly dismissed since solid ZnO or solid ZnS would have very minimal mass transfer in such a system since solid would be expected to accumulate on the bottom due to density differences. In performing research, it was anticipated (and later confirmed) that literature on such reactor systems would be limited since only companies that would like to keep their information classified perform such reactions at a large scale. Thus, a micro-scaled reactor that was executed for research purposes had to be considered and scaled up to the size of this process. Faculty in the Department of Chemical Engineering at Louisiana State University, Baton Rouge, had published findings that were very closely aligned with the concepts used for the model of this reactor ^[5.1.2.3]. Their findings had a substantial amount of missing information that would have improved specificity of this design process but nonetheless could be used with reasonable assumptions to fill in the gaps.

Reaction Kinetics

Gibson and Harrison's research analyzed the zinc oxide reaction with hydrogen sulfide in conversion to zinc sulfide ^[5.1.2.3]. Since zinc oxide is a solid power which is difficult to transfer through a reaction without serious interference by means of impellers or a solvent, a clever method of pellet carrying was used. These spherical pellets were coated with the solid reagent and, despite the high temperatures being discussed, were able to contain all of the solid species that react and convert. These pellets did not change in size and actually followed from the reactor with the desired solvent. The kinetics of this reaction were measured by visualizing the pellets as each holding a large number of very small solid reactant grains, assumed to be of a spherical geometry for coordinate simplification. The reaction rate considered was for an individual grain and was scaled up for a fixed amount of grains under the assumption that conversion did not vary from grain-to-grain or even pellet-to-pellet. This assumption was carried over to this model to go a step further, such that the diminishing volume of the zinc oxide grain was proportional to the diminishing concentration of reactant and therefore appearing concentration of product. In short, the following reaction rate was used ^[5.1.2.3]:

$$\frac{dr'_c}{dt} = \frac{a_s k'_s C_A}{\left[1 - \frac{a_s k'_s C_{s0} r'_c}{D_A} \left(1 - \frac{r'_c}{r'_s} \right) \right]} \quad (5.1.2.11)$$

Where r'_c was the radius of the grain, that is the amount of zinc oxide within a given grain. The kinetic rate constant, k'_s , was calculated using the correlation provided by Gibson ^[5.1.2.3]:

$$k'_s = k_0 e^{\frac{-E}{RT}} \quad (5.1.2.12)$$

The constants shown in this equation were listed in Table 5.1.2.4. The reaction rate (5.1.2.11) was the core reaction rate that was used to determine how fast the reaction proceeds to produce the desired product. The resulting reaction rate was adjusted in terms of the concentration of the hydrogen sulfide concentration since this was the limiting reactant. 100 percent conversion of this species was expected so this reaction was deemed complete when this reactant completely disappeared. The other reagents were calculated to be produced relative to the stoichiometric equations (5.1.2.1 and 5.1.2.2) above, such that water was produced on a 2:1 mol ratio to hydrogen sulfide. This was shown in the material balances section of the matlab code, found in Appendix G. The kinetics of the ignored reaction (5.1.2.1) were not used and so the hydrogen sulfide reaction serves as a rough estimate as to how much of the product is produced. It was assumed that there was no selectivity between these reactions such that both reactions occurred at an identical pace.

Energy Balances

Since, as mentioned, the heat of reaction was deemed significant and thermal behavior to be considerable, thermal energy balances had to be derived. To determine the thermal behavior of this system, the effects of the heat transfer fluid, heat of reaction, and heat capacity of the components in the reactor all had to be considered. Using a relationship provided by Folger for multiple reactions occurring in a plug-flow reactor, Equation 5.1.2.13 was derived [5.1.2.3]:

$$\frac{dT_r}{dV} = \frac{Ua(T_c - T_r) + \sum_{Ai} \Delta H_{Ri}}{\sum_i v_i C_{pi}} = \frac{Ua(T_c - T_r) + \sum_{Ai} \left(\int_{543}^{298} \sum n_c c_p dT + \sum n \Delta H_{f, products}^0 - \sum n \Delta H_{f, reactants}^0 + \int_{298}^{543} \sum n_c c_p dT \right)}{\sum_i v_i C_{pi}} \quad (5.1.2.13)$$

Using this reaction for a singular reaction, such as the case with this design, is done by simply ignoring the sigma component in the heat of reaction term such that only a single heat of reaction is accounted for. The thermal behavior of the coolant fluid is also of interest as from the assumption that heat is completely transferred, the temperature gained or lost by the reactor should mirror the thermal behavior of the heat transfer fluid, derived in Equation 5.1.2.14 [5.1.2.3]:

$$\frac{dT_c}{dV} = \frac{Ua(T_r - T_c)}{mC_p} \quad (5.1.2.14)$$

A heat transfer coolant of Dowtherm A was selected, as the overall heat transfer coefficient as shown in Table 5.1.2.4 was within the expected range of Dowtherm. The reactor energy balance equation was simplified tremendously since there was only one reaction that was being considered. The temperature difference was taken with respect to volume rather than length to account for the specific cylindrical geometry which allowed for the mass of the flows to be

considered. As a result of these two energy balances, temperatures for the reactor and temperatures for the coolant were found with respect to volume.

Reactor Assumptions

Before displaying the results of this design, a variety of assumptions were implemented that warrant brief discussion. Listed below is a table of general reactor specifications that can be found in the Matlab code given in full in Appendix G.

Table 5.1.2.4. Reactor/Species Specifications

Variable	Value	Units	Source
V_R , Reactor Volume	4200	L	Estimated from calculation
$\dot{m}_c$, Mass Flow of Coolant Fluid	260000	g/hr	Arbitrary
D_p , Diameter of Pellet	0.18	cm	[5.1.2.3]
D_R , Diameter of Reactor	$D_p \cdot 950$ $=3.43$	cm	Arbitrary
L , Length of Reactor	1.81	m	Calculated
Δr , Thickness of Reactor Wall	0.02	m	Arbitrary
U , Overall Heat Transfer Coefficient of Coolant Fluid	300	W/m ² -°C	estimated
$C_{p,c}$, Heat Capacity of Coolant Fluid	1.25	J/g-°C	estimated
T_i , Inlet Reactor Temperature	650	°C	Arbitrary
T_c , Temperature of Coolant Fluid	635	°C	Arbitrary
P , Reactor Pressure	3500	kPa	Specified
ZnO Flow Rate	2.35	kmol/hr	Aspen
H ₂ S Flow Rate	0.0825	kmol/hr	Aspen
Material of Construction	Stainless steel		[5.1.2.7]
k_o , Pre-exponential Constant	$9.46 \cdot 10^{-2}$		[5.1.2.3]
E , Activation Energy	7236	J/mol	[5.1.2.3]

The most notable variable of this table was the pressure of the reactor, assumed to be 35 kPa. It was unclear what pressure the reactor was run at in Gibson and Harrison's research ^[5.1.2.3]. What is promising is that ASPEN Plus displayed the same results for the outlet stream at the two different pressures (35kPa and atmospheric) which was likely due to the solid nature of the reactor. The next most notable variable that subsequently determined several other variables was the volume of the reactor. This volume was determined by converting the mass flow rates of the two reagents (ZnO and H₂S) into volumetric flow rates along with using a rough prediction of the space time from conversion data provided by Gibson and Harrison ^[5.1.2.3]. A rough estimate of the volume of this reactor was subsequently derived and applied for usage. The ratio of the reactor diameter to the pellet diameter was relatively large compared to what was expected. This value was chosen arbitrarily with consideration towards the fact that reagents were already at specified temperatures, allowing for a larger cylindrical radius. During the reiteration process, it was encouraging that the initial estimate of a volume slightly larger than the methanol reactor (4200 to 3500) was upheld. A temperature of 650°C was selected rather than the suggested temperature of 210°C. This value was selected because Gibson and Harrison indicated that kinetics were extremely unfavorable at temperatures less than 600°C such that residence times were painfully long ^[5.1.2.3].

Reactor Results and Discussion

Results were first compiled for the flow rates of the reactants in the two reactions along the reactor length, as shown in Figures 5.1.2.1, 5.1.2.2, and 5.1.2.3.

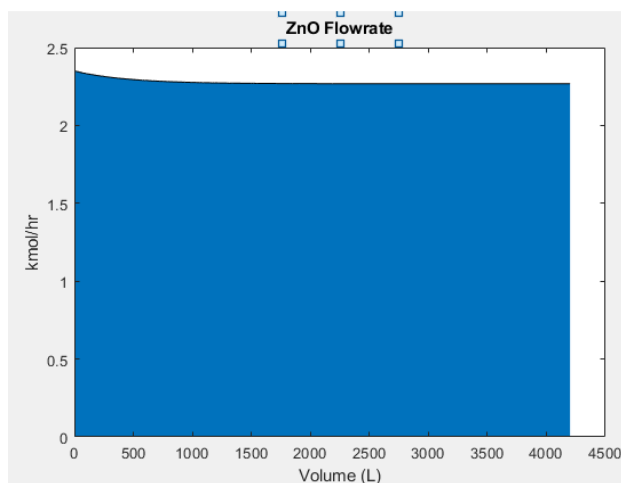


Figure 5.1.2.1 Flow rate of ZnO along the reactor (Reactor Volume = 4200 L)

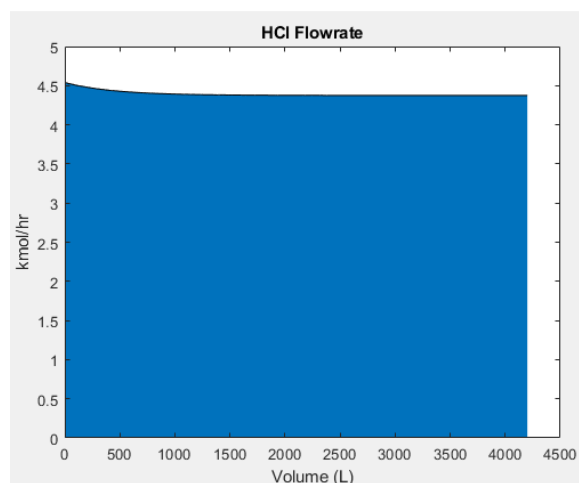


Figure 5.1.2.2 Flow rate of HCl along the reactor

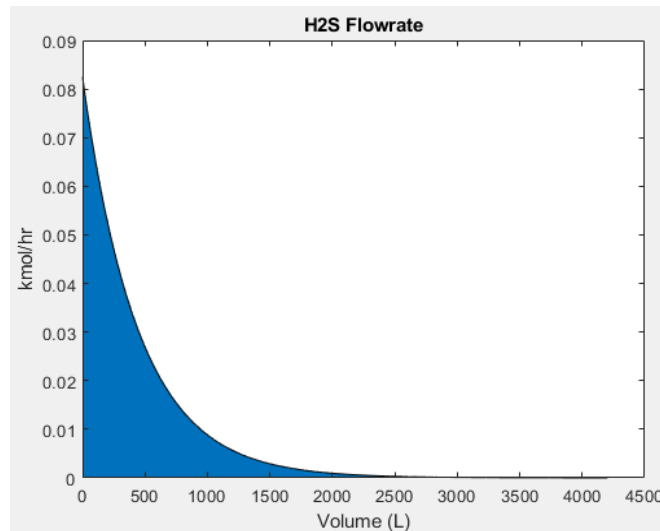


Figure 5.1.2.3 Flow rate of H_2S along the reactor

The flow rates of ZnO and HCl only decreased by a fraction along the reactor length, which was expected of this reaction since a substantially smaller amount of the limited reagent, H_2S was fed into the reactor. As a result of this difference, only a small amount of ZnO and HCl was required to obtain a hydrogen sulfide conversion of 100 percent. General principles of reaction kinetics suggest it generally becomes much more difficult to remove the last bit of reagent to reach 100 percent conversion. Figure 5.1.2.3 shows that the majority of the reactor volume was devoted towards removing the last fraction of hydrogen sulfide. Complete conversion was not actually achieved but was very close (99.9913%).

Next, the flow rates of the products were analyzed as shown in Figures 5.1.2.4, 5.1.2.5, and 5.1.2.6.

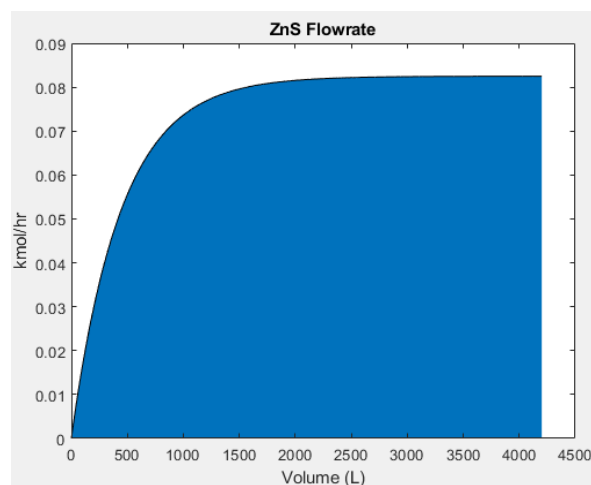


Figure 5.1.2.4 Flow rate of ZnS along the reactor

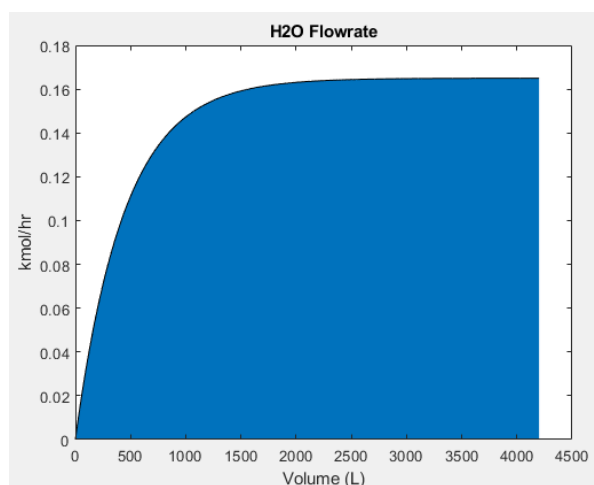


Figure 5.1.2.5 Flow rate of H_2O along the reactor

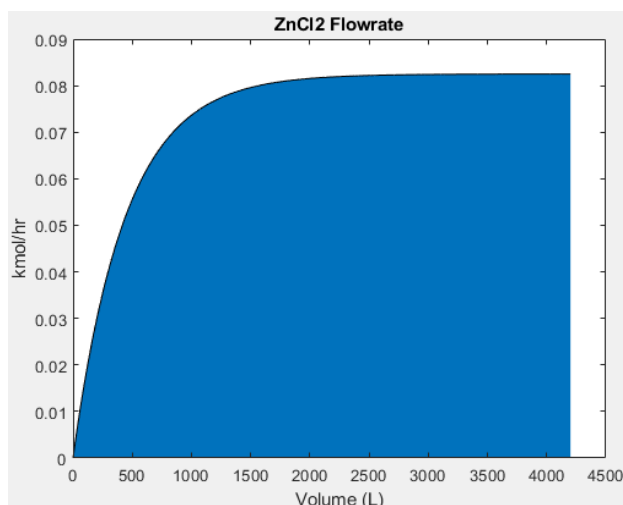


Figure 5.1.2.6 Flow rate of ZnCl_2 along the reactor

The flow rates as shown in these figures were expected to show an increasing trend as more product was accumulating the farther along the reactor, after more of the reaction had occurred. The trends showed exponential behavior such that the majority of conversion was reached in the early stage of the reactor while the last bit of product was produced in the later larger fraction of the reactor. The water flow rate was shown to be twice in magnitude as the other products which was due to the mentioned stoichiometry, as water was produced in a 1:1: mole ratio of hydrogen sulfide in two reactions.

Next, the temperature profiles of the reactor and coolant fluid were both derived as shown in Figures 5.1.2.7 and 5.1.2.8 below.

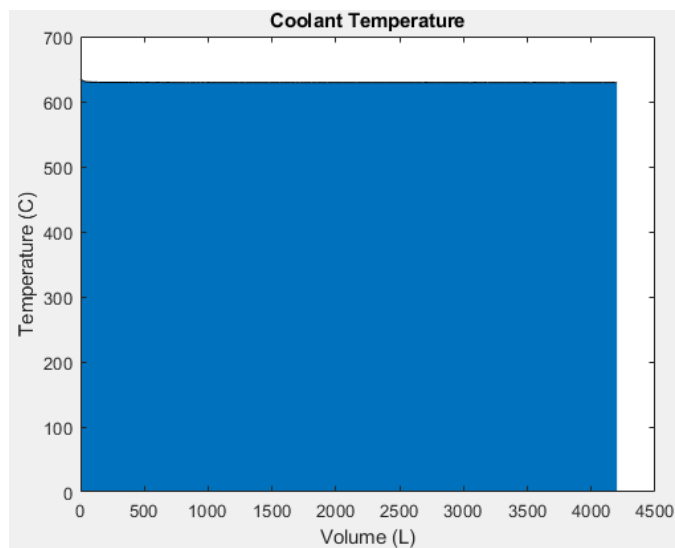


Figure 5.1.2.7 Coolant temperature along the reactor

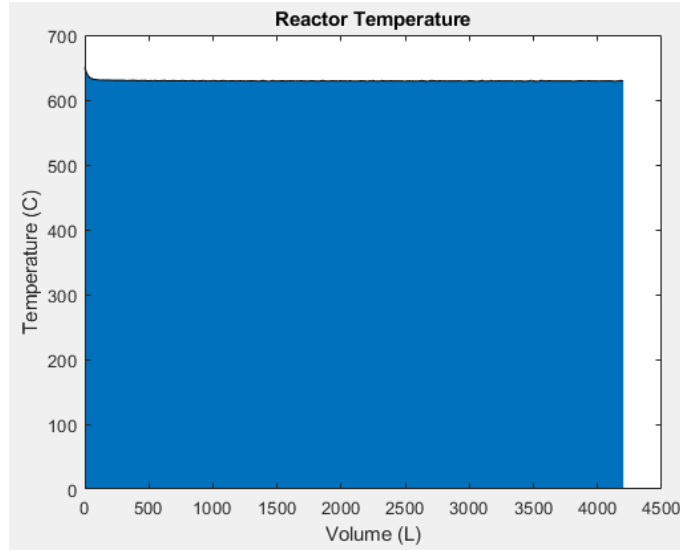


Figure 5.1.2.8 Reactor temperature along the reactor

These temperature profiles were iterated by changing the mass flow rate of coolant fluid. There was not much change observed in either graph as it was the goal of the heat transfer fluid to keep the reactor in its optimal kinetic range of 600 - 700°C so that the reaction occurred at its fastest rate. If no heat transfer fluid was provided, the reactor would have cooled from 600°C because of the endothermic heat of reaction. Thus, the coolant fluid was actually used to keep the reactor from cooling down, acting as a heating fluid instead. Provided below is a rough sketch of the reactor.

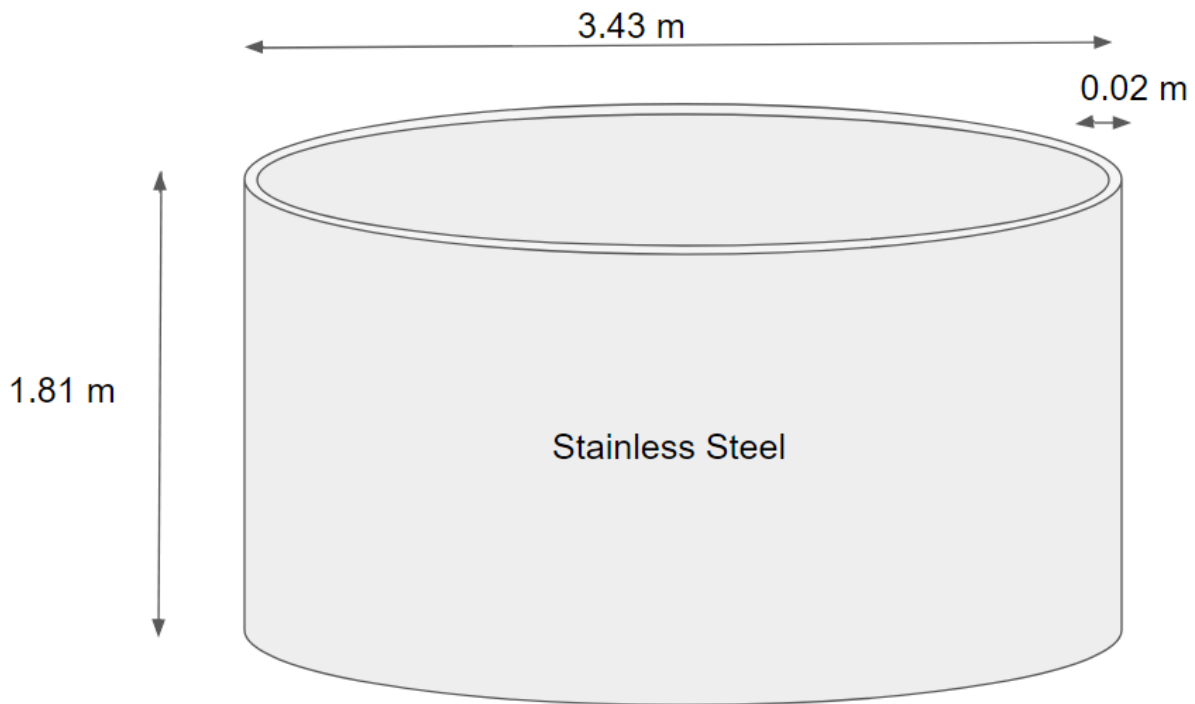


Figure 5.1.2.9 Zinc oxide reactor diagram

5.1.3 Methanol Fixed-Bed Reactor

Process Role

The role of the methanol reactor was to produce raw “dirty” methanol from synthesis gas. The syngas feed was mixed with a recycle stream before it entered a compressor where it was compressed isentropically to 80 bar. This stream then entered the reactor where carbon monoxide hydrogenation, carbon dioxide hydrogenation and water gas shift reactions occurred. The reactor was a multi-tube fixed bed reactor with copper-zinc oxide catalyst pellets filling the tubes. The reactor was cooled with a Dowtherm A coolant stream on the shell side of the reactor. The stoichiometry of these reactions were outlined in Table 5.1.3.1 and molar constants for all stream species are included in Table 5.1.3.2.

Table 5.1.3.1 Reactions

Reaction	Reaction Balance
1	$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$
2	$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$
3	$\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$

It was important to note that in reality, all three of the above reactions were reversible reactions. Therefore, for the sake of ideality they were modeled as such for the remainder of the methanol reactor design. This complicated the modeling process but also gave the best idea of how this reactor would operate in reality.

Table 5.1.3.2 Molar Constants (Felder and Rousseau 2005)^[5.1.3.1]

Component	MW (g/mol)
CO_2	44.01
H_2	2.016
CO	28.01
H_2O	18.02
CH_3OH	32.04
N_2	28.013

Heats of Reaction & Heat Capacity Calculations

Under standard conditions (T=298K), determining the heat of reaction was as simple as summing the heat of formations of the reactants multiplied by the respective stoichiometric coefficients and subtracting that from the heat of formation of the products multiplied by the respective stoichiometric coefficients. As these reactions were to be found at non-standard conditions (T=543K), the energy loss required to cool the reactants from 543K to 298K and the energy gained to heat the products from 298K to 543K also had to be accounted for in the heats of reactions.

The individual differences in heat for these steps could then be added up to yield the heats of reaction following the equation below.

$$\Delta H_{rxn} = \sum_1^3 \Delta H_n \quad (5.1.3.1)$$

ΔH_1 could be found using the following equation, where n was the stoichiometric coefficient of a reactant and c_p was the corresponding constant pressure heat capacity.

$$\Delta H_1 = \int_{543}^{298} \sum n c_p dT \quad (5.1.3.2)$$

ΔH_2 was, as stated before, the sum of the heats of formation of the products multiplied by the respective stoichiometric coefficient minus the sum of the heats of formation of the reactants multiplied by the respective stoichiometric coefficient as outlined in the equation below.

$$\Delta H_2 = \sum n \Delta H_{f, products}^o - \sum n \Delta H_{f, reactants}^o \quad (5.1.3.3)$$

ΔH_3 could be found similarly to ΔH_1 using the following, where n was the stoichiometric coefficient of a product and c_p was the corresponding constant pressure heat capacity.

$$\Delta H_3 = \int_{298}^{543} \sum n c_p dT \quad (5.1.3.4)$$

In order to calculate species heat capacities, coefficients were used as shown in Table 5.1.3.3.

Table 5.1.3.3 Heat Capacity Coefficients (Felder and Rousseau 2005)

	Heat Capacity Constants $c_p \text{ (kJ/molK)} = A + Bt + Ct^2 + Dt^3$				$c_p \text{ (kJ/molK)}$
Species	A * 10 ³	B * 10 ⁵	C * 10 ⁸	D * 10 ¹²	
CO ₂	36.11	4.233	-2.887	7.464	0.0455
H ₂	28.84	0.00765	0.3288	-0.8698	0.0290
CO	28.95	0.411	0.3548	-2.22	0.0302
H ₂ O	33.46	0.688	0.7604	-3.593	0.0358
CH ₃ OH	42.93	8.301	-1.87	-8.03	0.0638
N ₂	29	0.2199	0.5723	-2.871	0.0299

Heat capacity constants were taken for the gas phase of all species due to the high reaction temperature and fact that there was a pressure drop along the length of the reactor. For all of the above species, heat capacity as a function of temperature could be described by the equation $C_p = A + BT + CT^2 + DT^3$, with temperature in degrees Celsius.

In order to use the equations of heat capacity to determine ΔH_1 and ΔH_3 , the expressions for heat

capacity had to be integrated. $\Delta H_1 = \int_{543}^{298} \sum n_c c_p dT$. Thus, for the species in Table 5.1.3.1,

$$\Delta H_{1,i} = \int_{543}^{298} n_i * (A_i + B_i T + C_i T^2 + D_i T^3) dT \quad (5.1.3.5)$$

$$= n_i \left[\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=298K,i} - \left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right)_{T=543K,i} \right] \quad (5.1.3.6)$$

Integrated heat capacity values for each species at T = 298 K and T = 543 K were calculated and tabulated as shown in Table 5.1.3.4. For the purpose of the methanol reactions, nitrogen did not react and therefore was left out of the remainder of the calculations.

Table 5.1.3.4 Heat Capacity Integrals at Relevant Temperatures

Species	C_p at 298 K = 25 C_p , kJ/mol-K	C_p at 543 K = 270 C_p , kJ/mol-K
CO_2	0.915	11.113
H_2	0.721	7.810
CO	0.725	7.986
H_2O	0.838	9.330
CH_3OH	1.099	14.483

With these values calculated, ΔH_1 and ΔH_3 could be determined using the following formulas.

$$\Delta H_1 = \sum n_{i(\text{reactants})} * (C_{p,298 K} - C_{p,533 K})_i \text{ and } \Delta H_3 = \sum n_{i(\text{products})} * (C_{p,533 K} - C_{p,298 K})_i \quad (5.1.3.7)$$

One sample calculation has been provided for the first reaction (Reaction 1, as given in Table 5.1.3.1), shown below. The complete set of ΔH_1 and ΔH_3 final values are included in Table 5.1.3.5.

$$\Delta H_{1,1} = [(0.725 - 7.986) + 2 * (0.721 - 7.810)] = -21.439 \text{ kJ/mol} \quad (5.1.3.8)$$

$$\Delta H_{3,1} = (14.483 - 1.099) = 13.384 \text{ kJ/mol} \quad (5.1.3.9)$$

Table 5.1.3.5 ΔH_1 and ΔH_3 values for all Equations

Reaction	ΔH_1 kJ/mol	ΔH_3 kJ/mol
1	-21.439	13.384
2	-17.286	15.752
3	-31.464	21.875

To calculate ΔH_2 , the standard heats of formation were required. For the purpose of our calculations the reactants were cooled to 298 K and the reactions happened at this standard

temperature. Table 5.1.3.6 provided a summary of the heats of formation for all eight compounds at the standard temperature of 298 K.

Table 5.1.3.6 Heat of Formation at Reaction Temperature (Felder and Rousseau 2005)

Species	Reaction Temperature (K)	Heat of Formation (kJ/mol)
CO_2	298	-393.5
H_2	298	0
CO	298	-110.52
H_2O	298	-241.83
CH_3OH	298	-201.2

To calculate the change in enthalpy that occurred due to the reaction, the equation used taken the form $\Delta H_2 = \sum n\Delta H_{f,products}^o - \sum n\Delta H_{f,reactants}^o$, with the superscript nought indicating that the heats of formation were taken at the standard temperature of 298 K. A sample calculation has again been provided below for reaction 1.

$$\begin{aligned}\Delta H_{2,1} &= [1(-201.2)] - [1(-110.52) + 2(0)] \\ &= -90.68 \text{ kJ/mol}\end{aligned}\tag{5.1.3.10}$$

The same process was repeated for each of the reactions, and the values calculated for ΔH_2 for all the reactions were summarized in Table 5.1.3.7.

Table 5.1.3.7 Summed Heat of Formations for Each Reaction

Reaction	ΔH_2 (kJ/mol)
1	-90.68
2	41.15
3	-49.53

The three ΔH values were summed for each reaction to find the overall heat of each reaction. A negative value indicated that the reaction was exothermic and produced heat while a positive

value indicated a reaction that was endothermic and consumed heat. This calculation setup was shown below for clarification. It was important to note an assumption that the heat of reaction for all components was a constant at the 543 K reaction temperature along the length of the reactor.

$$\text{Heat of Reaction}_{\text{Reaction, i}} = \Delta H_{1,i} + \Delta H_{2,i} + \Delta H_{3,i} \quad (5.1.3.11)$$

Table 5.1.3.8 Final Enthalpies of Reaction at the Reactor Temperature T=543 K

Reaction	ΔH_1 (kJ/mol)	ΔH_2 (kJ/mol)	ΔH_3 (kJ/mol)	Heat of Reaction (kJ/mol)
1	-21.439	-90.68	13.384	-98.735
2	-17.286	41.15	15.752	39.616
3	-31.464	-49.53	21.875	-59.118

Model Approach & Equation

In order to model this reactor, appropriate reaction kinetics had to be found in the literature. The kinetics from Kinetics of Methanol Synthesis from Carbon Dioxide Hydrogenation over Copper-Zinc Oxide Catalysts (Falk et. al, 2017) were chosen as they described the reactions with the same catalyst and reactor type^[5.1.3.3]. The rate equations used were introduced in Table 5.1.3.9. As mentioned earlier, kinetic modeling was done taking into account the fact that these reactions were reversible in reality.

Table 5.1.3.9 Methanol Reaction Rate Equations (Falk et. al, 2017)

Methanol Reaction	Rate Equation (mol/s)
1. $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$	$r_1 = k_1 b_{\text{CO}} \left\{ \frac{p_{\text{CO}} p_{\text{H}_2}^{3/2} - \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{H}_2}^{1/2} K_1}}{(1 + b_{\text{CO}} p_{\text{CO}} + b_{\text{CO}_2} p_{\text{CO}_2}) [p_{\text{H}_2}^{1/2} + (\frac{b_{\text{H}_2\text{O}}}{b_{\text{H}_2}^{1/2}}) p_{\text{H}_2\text{O}}]} \right\}$
2. $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	$r_2 = k_2 b_{\text{CO}_2} \left\{ \frac{p_{\text{CO}_2} p_{\text{H}_2} - \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{K_2}}{(1 + b_{\text{CO}} p_{\text{CO}} + b_{\text{CO}_2} p_{\text{CO}_2}) [p_{\text{H}_2}^{1/2} + (\frac{b_{\text{H}_2\text{O}}}{b_{\text{H}_2}^{1/2}}) p_{\text{H}_2\text{O}}]} \right\}$

3. $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$	$r_3 = k_3 b_{\text{CO}_2} \left\{ \frac{p_{\text{CO}_2} p_{\text{H}_2}^{3/2} - \frac{p_{\text{CH}_3\text{OH}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{3/2} K_3}}{(1 + b_{\text{CO}} p_{\text{CO}} + b_{\text{CO}_2} p_{\text{CO}_2}) [p_{\text{H}_2}^{1/2} + (\frac{b_{\text{H}_2\text{O}}}{b_{\text{H}_2}^{1/2}}) p_{\text{H}_2\text{O}}]} \right\}$
---	--

For these expressions, k_n corresponded to kinetic constants for reactions 1-3, K_n corresponds to equilibrium constants for each reaction and b_i corresponds to the adsorption constant of species i as shown in Tables 5.1.3.10, 5.1.3.11 and 5.1.3.12 respectively. p_i referred to the partial pressure of species i in bar. It is important to note that temperature in the constant equations was in Kelvin.

Table 5.1.3.10 Kinetic Constants (Falk et. al, 2017)

Expression	Kinetic Constant
k_1	$4.89 \times 10^7 \exp(\frac{-113000}{RT}) \quad (\frac{\text{mol}}{\text{s} * \text{bar}})$
k_2	$9.64 \times 10^{11} \exp(\frac{-152900}{RT}) \quad (\frac{\text{mol}}{\text{s} * \text{bar}^{1/2}})$
k_3	$1.09 \times 10^5 \exp(\frac{-87500}{RT}) \quad (\frac{\text{mol}}{\text{s} * \text{bar}})$

Table 5.1.3.11 Equilibrium Constants (Falk et. al, 2017)

Expression	Equilibrium Constant
K_1	$10^{\frac{5139}{T} - 12.621}$
K_2	$10^{\frac{-2073}{T} - 2.029}$
K_3	$10^{\frac{3066}{T} - 10.592}$

Table 5.1.3.12 Adsorption Constants (Falk et. al, 2017)

Expression	Adsorption Constant
b_{CO}	$2.16 \times 10^{-5} \exp(\frac{46800}{RT}) \text{ (bar}^{-1}\text{)}$
b_{CO_2}	$7.05 \times 10^{-7} \exp(\frac{61700}{RT}) \text{ (bar}^{-1}\text{)}$
$\frac{b_{H_2O}}{b_{H_2}^{1/2}}$	$6.37 \times 10^{-9} \exp(\frac{84000}{RT}) \text{ (bar}^{-1/2}\text{)}$

This reactor could be modeled as many parallel tubes filled with catalyst beads with enough space in between to allow the syngas to flow and react. The tubes were assumed to be 1 inch or 0.0254 meter inner diameter filled with catalyst pellets with $\frac{1}{8}$ inch or 0.003175 meter diameter. The voidage of the catalyst bed was assumed to be 0.41, as was reported in Falk et. al.

In order to begin to model the reactor in MATLAB, differential equations had to be developed governing the species material balances, coolant energy balance, reactor energy balance and pressure drop along the length of the reactor. All differential equations were integrated with respect to the volume of the reactor so that solutions could be plotted over the length of the reactor.

Species Mole Balance

The first step was to develop mole balances for all of the reactant species that passed through the reactor in the form of rates of production. These rates would utilize the reaction rates outlined in Table 5.1.3.9 and were listed below:

$$r_{CO_2} = -r_2 - r_3 \quad (5.1.3.12)$$

$$r_{CH_3OH} = r_1 + r_3 \quad (5.1.3.13)$$

$$r_{H_2} = -2r_1 - r_2 - 3r_3 \quad (5.1.3.14)$$

$$r_{CO} = -r_1 + r_2 \quad (5.1.3.15)$$

$$r_{H_2O} = r_2 + r_3 \quad (5.1.3.16)$$

Based on what is known about packed bed reactors, the mole balance for any one given species is given by $r_i = \frac{dF_i}{dV}$. Therefore, if one wished to express them in the form dF/dV , a simple substitution gave:

$$\frac{dF_{CO_2}}{dV} = -r_2 - r_3 \quad (5.1.3.17)$$

$$\frac{dF_{CH_3OH}}{dV} = r_1 + r_3 \quad (5.1.3.18)$$

$$\frac{dF_{H_2}}{dV} = -2r_1 - r_2 - 3r_3 \quad (5.1.3.19)$$

$$\frac{dF_{CO}}{dV} = -r_1 + r_2 \quad (5.1.3.20)$$

$$\frac{dF_{H_2O}}{dV} = r_2 + r_3 \quad (5.1.3.21)$$

It was important to note that while there was nitrogen present in the syngas, there was no mole balance for nitrogen as it was neither produced nor consumed in any of the reactions. Nitrogen was still included in the model as it was important for the energy balances and pressure drop.

Energy Balances

Equation 4 presented the thermal energy balance for a PFR and could be used to model the reactor temperature for a multi-tube packed bed catalytic reactor. The difference between the temperature of the reactor and the coolant was multiplied by the heat transfer coefficient and integrated over the reaction area to give us the total heat transferred. A constant heat transfer coefficient of $300 \frac{W}{m^2 K}$ was assumed for this reactor. The heat transferred was also equal to the difference of the enthalpy of the product leaving the system and the enthalpy of the feed entering the system. Fogler explained how to manipulate this equality by differentiating with respect to volume. a was the heat exchange area per unit volume^[5.1.3.2]. This gave the form used here.

$$\frac{dT_r}{dV} = \frac{Ua(T_c - T_r) + \sum_{Ai} r_{Ai} \Delta H_{Ri}}{\sum_i C_{Pi}} = \frac{Ua(T_c - T_r) + \sum_{Ai} \left(\int_{543}^{298} \sum_p n c_p dT + \sum n \Delta H_{f, products}^0 - \sum n \Delta H_{f, reactants}^0 + \int_{298}^{543} \sum_p n c_p dT \right)}{\sum_i C_{Pi}} \quad (5.1.3.22)$$

The energy absorbed by the coolant could be expressed as a product of its mass flow rate, heat capacity and change in temperature as well as the difference between the temperature of the reaction and the coolant multiplied by the heat transfer coefficient over a certain area. Mass flow rate of coolant was arbitrary and its value was reported later in the model results. Rearranging this equation and rewriting in terms of volume gave equation 5.1.3.23. The numerator of this equation was equal to the numerator expressed in the dT/dV equation above, as the reactor was adiabatic.

$$\frac{dT_c}{dV} = \frac{Ua(T_r - T_c)}{mC_p} \quad (5.1.3.23)$$

Pressure Drop

The pressure was not constant throughout the length of the tube and as such, the Ergun equation (Eqn 5.1.3.24) was needed. The Ergun equation was manipulated to be expressed in terms of volume as opposed to the length of the tube. Equations 5.1.3.25 and 26 were combined to give equation 5.1.3.27 in terms of volume.

$$\frac{dP}{dz} = - \frac{(1-\phi)v}{D_p \phi^3 A_c} \left[150 \frac{(1-\phi)\mu}{D_p} + 1.75 \frac{\rho v}{A_c} \right] \quad (5.1.3.24)$$

$$\frac{dz}{dV} = \frac{1}{A_c} \quad (5.1.3.25)$$

$$\frac{dz}{dV} \frac{dP}{dz} = - \frac{(1-\phi)v}{D_p \phi^3 A_c} \left[150 \frac{(1-\phi)\mu}{D_p} + 1.75 \frac{\rho v}{A_c} \right] \frac{1}{A_c} \quad (5.1.3.26)$$

$$\frac{dP}{dV} = - \frac{(1-\phi)v}{D_p \phi^3 A_c^2} \left[150 \frac{(1-\phi)\mu}{D_p} + 1.75 \frac{\rho v}{A_c} \right] \quad (5.1.3.27)$$

These differential equations were inputted to MATLAB and solved simultaneously with the parameters outlined in Table 5.1.3.13.

Table 5.1.3.13 Model Parameters

Symbol	Definition	Value	Comments
Cp_c	Heat capacity of coolant	$2.25 \frac{J}{gK}$	Found at 270° C (Engineering Toolbox)
D	Inner tube diameter	0.0254 m	Problem statement
D_p	Catalyst particle diameter	0.003175 m	Heuristic - Catalyst diameter ~ 1/8 tube diameter
D_o	Outer tube diameter	0.0314 m	Assuming quarter inch thick tubes
m_c	Mass flowrate of coolant	1,000,000 $\frac{kg}{hr}$	Arbitrary
R	Gas constant	$3.814 \frac{J}{molK}$	
U	Coolant overall heat transfer coefficient	$300 \frac{W}{m^2K}$	Assumption for dowtherm A
v	Velocity of gas	$20 \frac{m}{s}$	Arbitrary

ρ	Gas density	$16.68 \frac{kg}{m^3}$	From HYSYS modeling
ρ_c	Catalyst density	$0.44 \frac{g}{cm^3}$	Falk et al.
ϕ	Catalyst porosity	0.41	Falk et al.
ϕ_b	Bed porosity	0.41	Falk et al.
μ	Gas viscosity	2.29E-08	From HYSYS modeling
Catalyst	Copper-Zinc Oxide		Falk et al.

Model Results and Discussion

MATLAB code (provided in Appendix H) reported several figures with essential information validating the reactor's design. The following five graphs report the change in molar flow rate of the five reactive species over the length of the reactor.

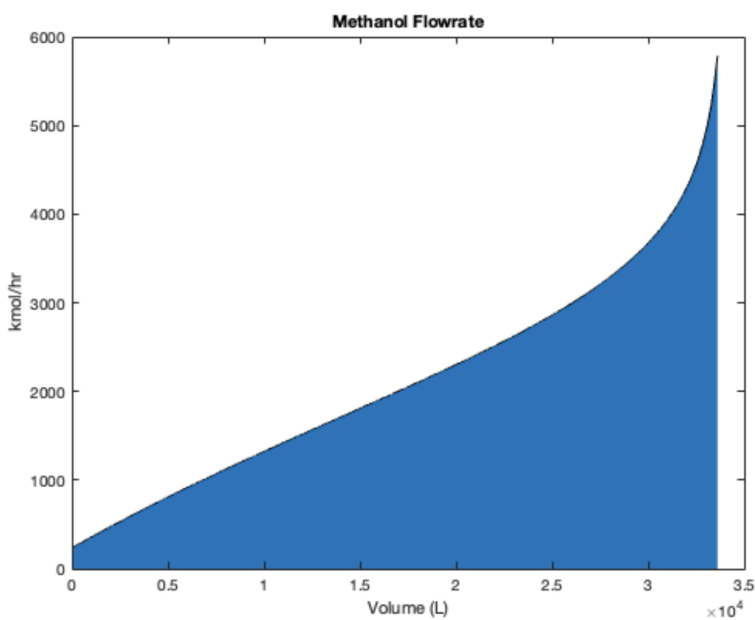


Figure 5.1.3.1 Methanol Flow Rate vs. Reactor Volume

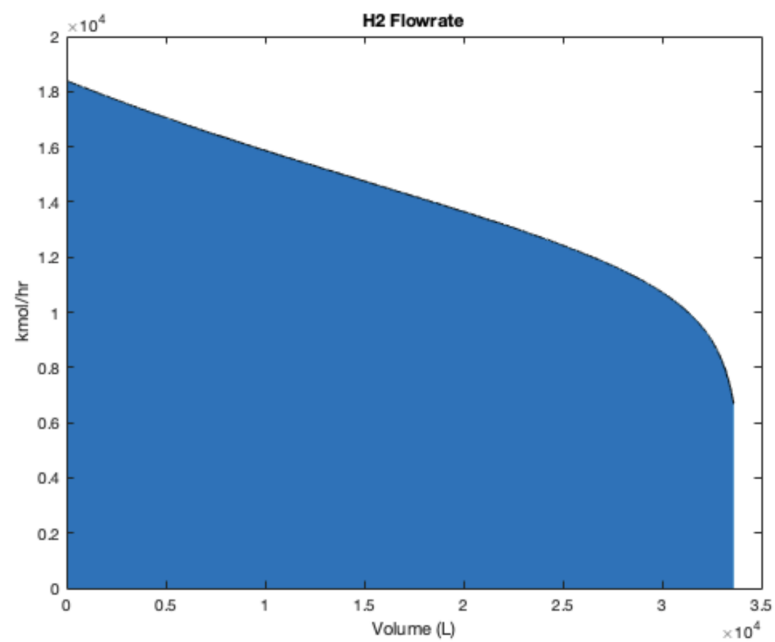


Figure 5.1.3.2 Hydrogen Flow Rate vs. Reactor Volume

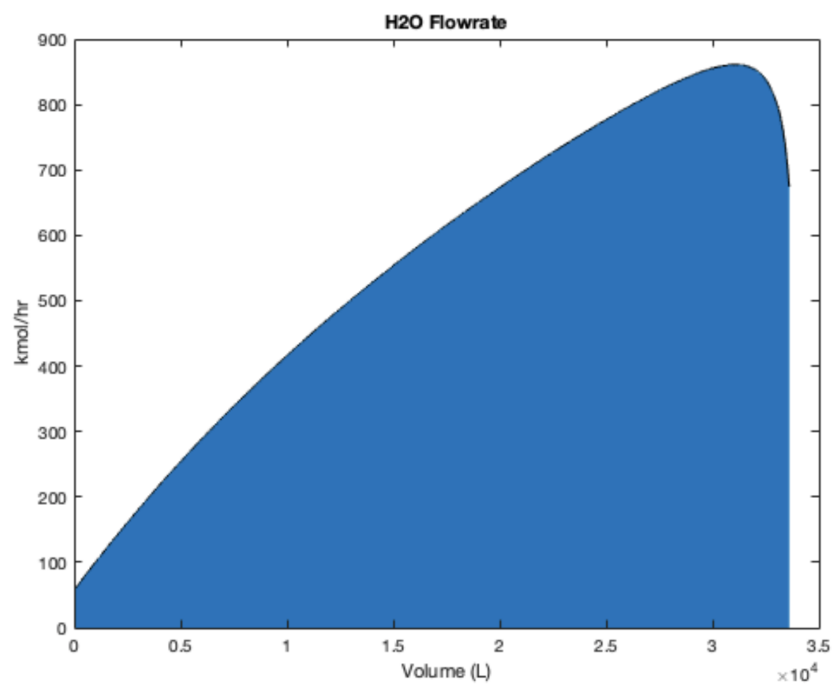


Figure 5.1.3.3 Water Flow Rate vs. Reactor Volume

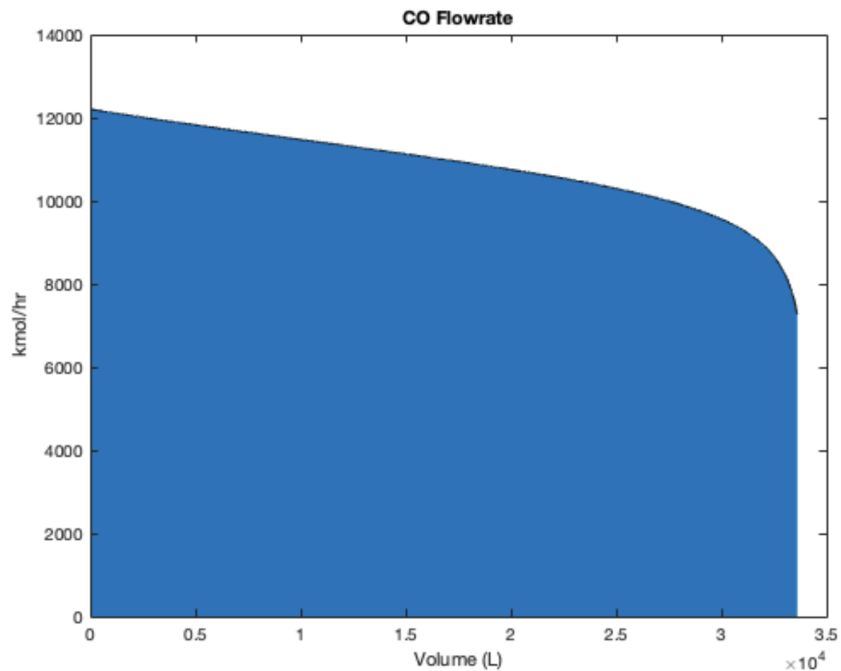


Figure 5.1.3.4 Carbon Monoxide Flow Rate vs. Reactor Volume

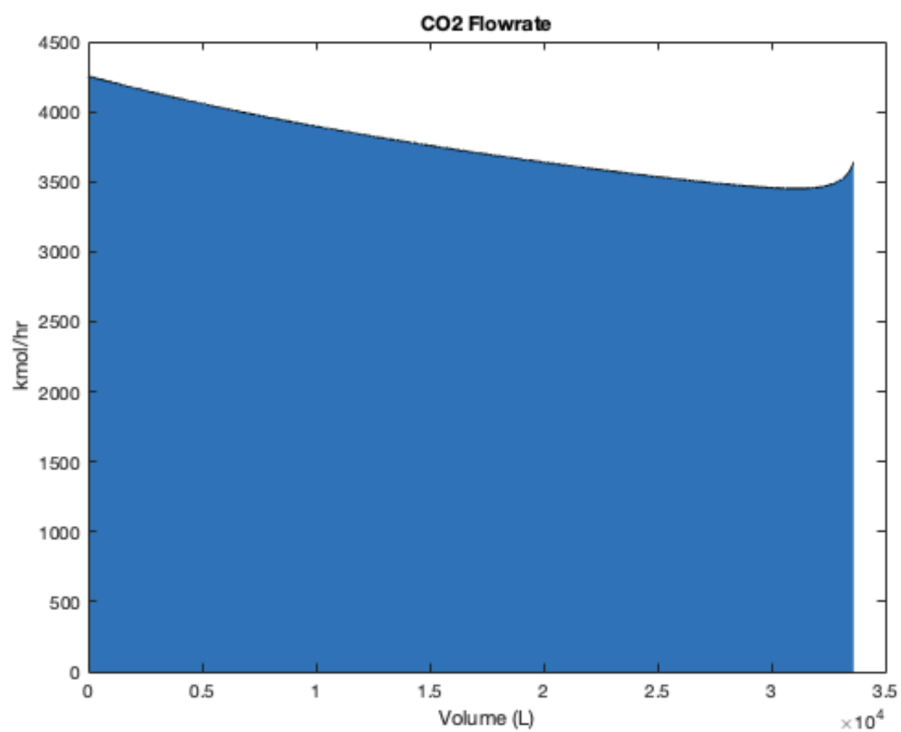


Figure 5.1.3.5 Carbon Dioxide Flow Rate vs. Reactor Volume

The next three figures showed the physical properties over the length of the reactor.

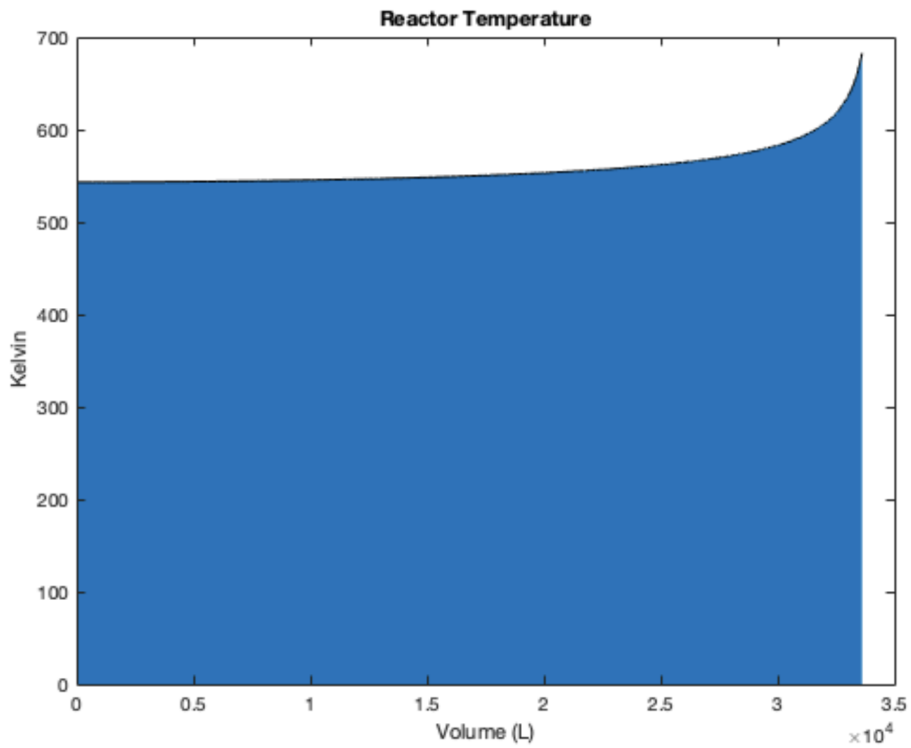


Figure 5.1.3.6 Reactor Temperature vs. Reactor Volume

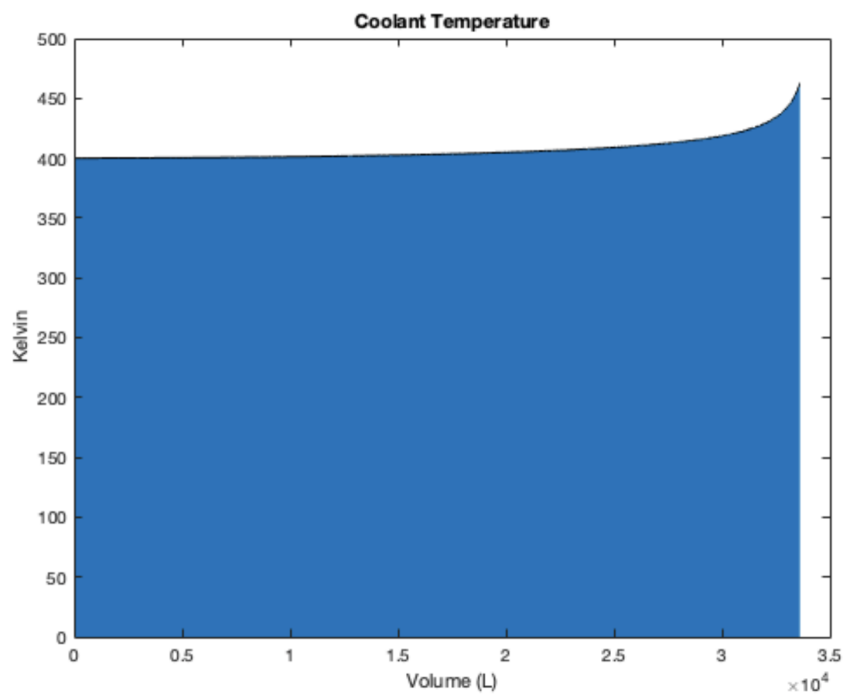


Figure 5.1.3.7 Coolant Temperature vs Reactor Volume

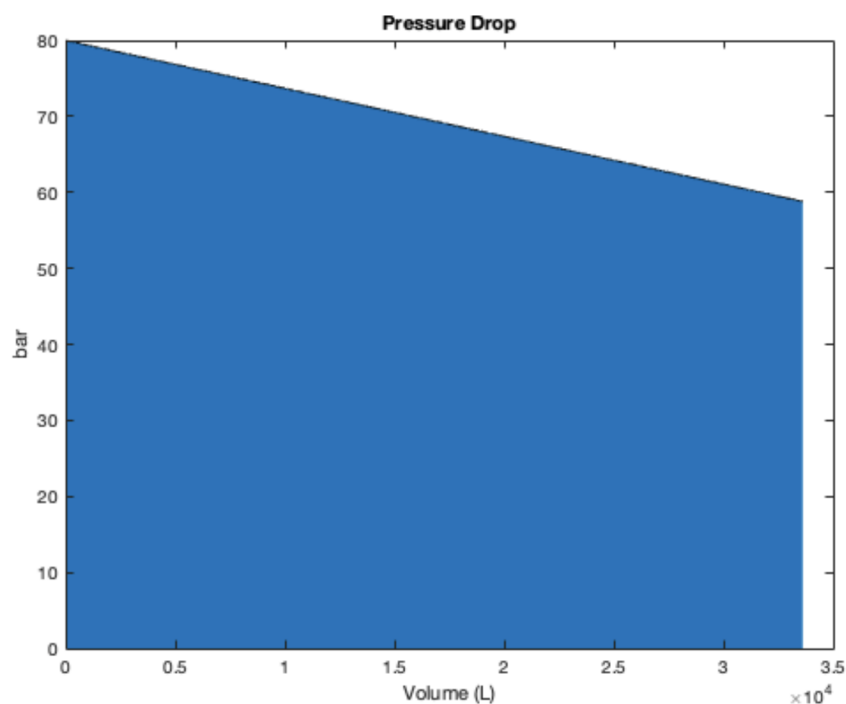


Figure 5.1.3.8 Pressure vs Reactor Volume

By looking at these plots, a better understanding could be obtained about what was happening inside the reactor. The most important metric to keep in mind when designing the methanol reactor was ensuring that enough methanol was produced to meet the demand. This was mainly what dictated how large the reactor was designed to be. From Figure 5.1.3.1, it was clear that the required $5,729 \frac{\text{kmol}}{\text{hr}}$ methanol flow rate that was found in ASPEN Plus was met and exceeded with a simulated value of 5,785. Figures 5.1.3.2, 4 and 5 showed that the reactants decreased over the length of the reactor, which was to be expected if the reactions proceeded forwards. Figure 5.1.3.3 showed that water was being produced over most of the reactor's length until the WGS reaction's equilibrium shifted backwards briefly. Figures 5.1.3.6 and 7 show how the heat produced from the highly exothermic reactions was managed with heat transfer between the reactor and coolant. Finally, Figure 5.1.3.8 showed the pressure drop over the length of the reactor.

The length of the reactor could be found by taking the volume of the catalyst and dividing by the total cross sectional area. Final reactor length was shown in Table 5.1.3.14.

$$L = \frac{V}{A_{c, \text{total}}} \quad (5.1.3.28)$$

The mass of the catalyst was found by calculating the combined volume of all of the tubes, multiplying it by one minus the bed porosity and then by the density of the catalyst. Mass of catalyst was shown in Table 5.1.3.14.

$$m_c = \frac{D^2}{4} \pi L * (1 - \phi_b) * \rho_c \quad (5.1.3.29)$$

A stainless steel alloy (typically with chromium, nickel, and molybdenum) was selected as the construction material for this reactor due to the fact that there were no corrosive species and the temperature of the reactor stayed relatively low. Figure 5.1.3.8 provided a basic sketch of the dimensions of the methanol reactor as designed in this section of the report.

Table 5.1.3.14 Methanol Reactor Modeling Results

Variable	Value	Units
Reactor volume	33.61	m^3
Space time	0.28	s
Tube length	1.74	m
Mass of catalyst	8724.64	kg
Material of construction	Stainless steel	--
Number of reaction tubes	38,216	--

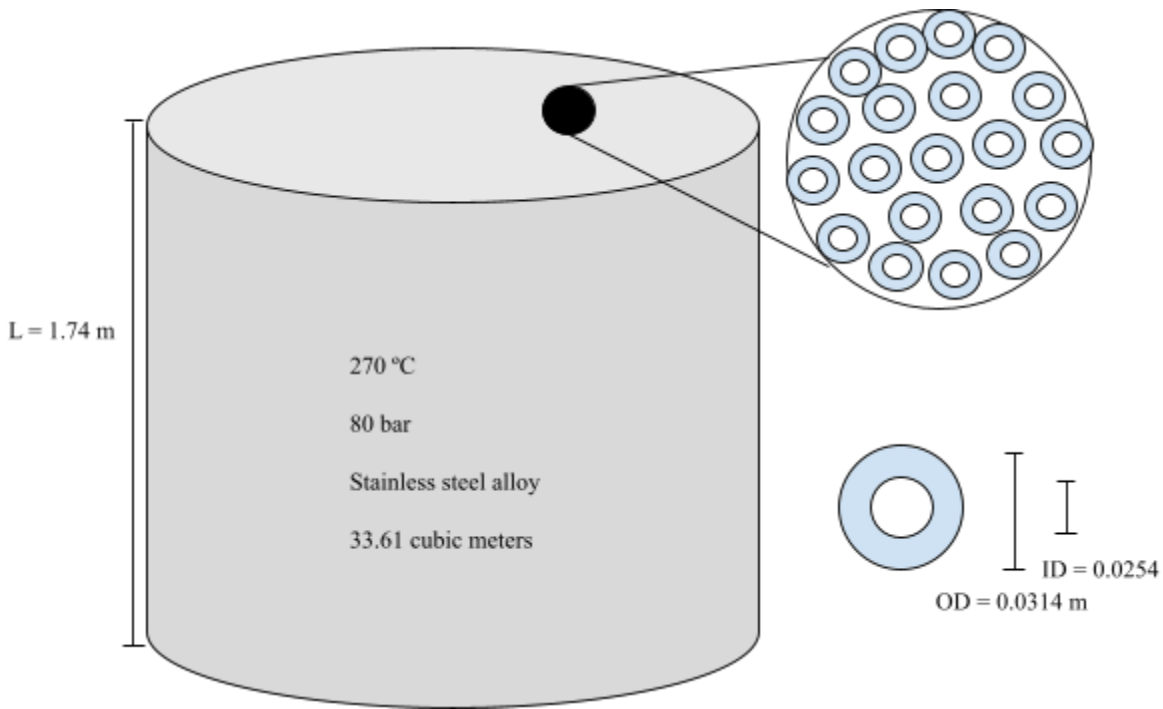


Figure 5.1.3.1 Methanol Reactor Design

5.2 Separators

5.2.1 Cyclones

One way of modeling a cyclone separator was to use a standard geometry that gave the ratios of the dimensions shown in Figure 5.2.1.1. Leith and Mehta (1972)^[5.2.1.1] have identified three recommended duties - high efficiency, high throughput, or general purpose. There was a tradeoff between efficiency and throughput in any given design. A high efficiency cyclone will process approximately half of the gas of a high throughput design with the same operating pressure, diameter, and overall height. Therefore, according to the needs of this process, we will choose a general purpose design with moderate efficiency and throughput.

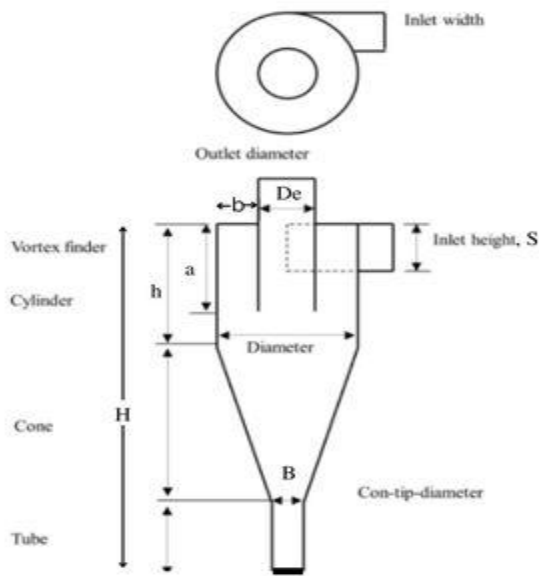


Figure 5.2.1.1: Dimensions of the cyclone separators, Park & Go (2020)^[5.2.1.2]

Dimension ratios were suggested for each of the recommended duties. Each of the cyclone measurements were expressed as a product of a dimension ratio and the cylinder diameter. The dimension ratios used for the general purpose duty, taken from Swift (1969)^[5.2.1.3], are given below:

Table 5.2.1.1 Dimension Ratios

Ratio	Symbol	Value
D	-	1
a/D	K_H	0.5
b/D	K_B	0.25
De/D	K_S	0.6
S/D	K_i	0.5
h/D	K_L	1.75
H/D	K_Z	2
B/D	K_D	0.4

Some physical properties of the inlet stream were also required. These were used in subsequent calculations to account for the effect of friction on characteristic velocities, the critical diameter, and the pressure drop. After that, the approach was to trial different D values, until the cut-off diameter and pressure drop was found. The cut off diameter is the diameter of particles at which half are separated out and is usually estimated through Lapple's model, shown below:

$$d_c = \sqrt{\frac{9\mu b}{2\pi N_e V_i (\rho_v - \rho_g)}} \quad (5.2.1.1)$$

where b is the inlet width of the cyclone, Vi is the inlet velocity of the gas, and Ne is the number of effective turns of the particle within the cyclone. To minimize the number of unknowns that are required to solve for, a simplified regression model developed by Demir et al. (2020) [5.2.1.4] was chosen.

$$d_c = a_1 K_b + \frac{a_2}{V_i} + \frac{a_3}{\rho_p} + a_4 \quad (5.2.1.2)$$

$$d_c = (0.25 * D * a_1) + \frac{a_2}{V_i} + \frac{a_3}{\rho_p} + a_4 \quad (5.2.1.3)$$

a₁ - a₃ are regression coefficients, given in the Table 5.2.1.2.

Table 5.2.1.2 Regression Coefficients

Coefficient	Value
a ₁	0.319
a ₂	1.095
a ₃	1.276

This regression model was chosen due to its high reliability. The R² value reported was 0.9969. To simplify the calculation of d_c for each iteration of the cutoff diameter, an Excel spreadsheet was used by industry professionals that had the equations built in for friction coefficients, characteristic velocities, and pressure drop.

To summarize, the physical constants obtained from ASPEN or estimated are given in the Table 5.2.1.3. D and the cutoff diameter were then simultaneously solved for, after which all other column dimensions could be found. To calculate the cut-off diameter, pressure drop across the cyclone and the overall efficiency in the form of the cut-off diameter need to be specified.

Table 5.2.1.3 Physical Constants

Property	Value	Units	Source
Gas flow rate	12406.67	m ³ /hr	ASPEN Plus
Dust load	0.01099	g/cm ³	ASPEN Plus
Gas viscosity	2.30 x 10e-5	Pa s	Engineering Toolbox source
Gas density	0.005106	g/cm ³	ASPEN Plus
Solid density	1.5	g/cm ³	Average density of cellulose and lignin

The D value for CYCLONE was found to be 2.25 meters. The overall cyclone design parameters are summarized in Table 5.2.1.5.

Table 5.2.1.5 Dimensions of CYCLONE

Dimension	Length / m
a	1.125
b	0.5625
De	1.35
S	1.125
h	3.934
H	4.5
B	0.9

ZN-SPLIT was also modeled as a cyclone as it separated solid zinc particles from the crude syngas. The same method as detailed for the CYCLONE was used. The same geometry was chosen.

The physical constants used for ZN-SPLIT are given in Table 5.2.1.4.

Table 5.2.1.4 Physical Constants for ZN-SPLIT

Property	Value	Units	Source
Gas flow rate	238565.17	L/min	ASPEN Plus
Dust load	0.0102	g/cm ³	ASPEN Plus
Gas viscosity	2.30 x 10e-5	Pa s	Engineering Toolbox source
Gas density	0.0102	g/cm ³	ASPEN Plus
Solid density	4.531	g/cm ³	ASPEN Plus

Similarly, D was found to be 6.5 m, and the remaining dimensions were estimated and are shown in Table 5.2.1.5:

Table 5.2.1.5 ZN-Split Dimensions

Dimension	Length / m
a	3.25
b	1.625
De	3.9
S	3.25
h	11.375
H	13
B	2.6

5.2.2 Distillation Columns

Two separators were modeled as distillation columns: VL-SEP, the knock out drum used in the raw methanol production unit, and the downstream methanol production unit, DISTIL.

Additionally, the reboilers and condensers were modeled as heat exchangers. VL-SEP took in a feed stream of dirty methanol mixed with water, and other gas streams. The output streams were split into three streams, with one being flared. The next distillation columns were modeled in several different ways: using an ASPEN HYSYS shortcut column, a full column, or making the relevant calculations by hand. To follow are the hand calculations used to design the downstream methanol production unit.

The first step was to obtain the compositions of the feed, distillate, and the bottoms. These values were obtained from the ASPEN HYSYS simulation of the downstream production plant. Next, the K values for each of the components were obtained from HYSYS. These values were required to determine the light and heavy keys, as well as where the components that are not light and heavy keys are retrieved. Water was chosen to be the heavy key, as 99.81% of it was recovered in the bottoms. Methanol was then chosen to be the light key as its K value is higher than water but lower than the remaining components. All the other components - hydrogen, methane, CO, CO₂, and nitrogen were assumed to have 100% recovery in the distillate as their K values are higher than methanol.

Now that the keys had been assigned, the next step was to determine the pressure calculations for the column. The bubble point pressure for the distillate stream was obtained from HYSYS, and was found to be 20.78 psi. As this value is smaller than 30 psi, Figure 9.9 of Seider et al^[5.2.2.1] was used to simplify our calculations, and assume that we use a total condenser. The pressure of the distillate was set to 30 psi. To estimate the pressure drop across the column, HYSYS's estimate for the full column's number of trays - 13 - and the pressure drop estimate across each tray of 1 psi was used, for a total pressure drop of 13 psi. Heuristic 31 states that the pressure drops in the condenser and the reboiler can be estimated as 1.5 psi each. Summing these values, a column pressure drop of 16 psi, and the pressure at the condenser of 46 psi were found.

To find all other column specifications, the Fenske-Underwood-Gilliland method was used. In order to determine the minimum number of stages, the Fenske equation was used.

$$N_{min} = \frac{\log\left(\frac{D_{LK}}{D_{HK}} \times \frac{B_{LK}}{B_{HK}}\right)}{\log(\alpha_{LK, HK})_{avg}} \quad (5.2.2.1)$$

Mole fractions of the light and heavy key were determined from HYSYS, and relative volatility values were calculated by finding the ratios of the K values at the distillate compared to the bottoms; the geometric averages were taken for the relative volatility of the light and heavy key in the distillate and the bottom. The minimum number of trays was then calculated to be 17. The minimum reflux ratio was then estimated using the Underwood equation. q is the amount of saturated liquid per mole of feed on the feed tray. This value was calculated from the full column model of the distillation column on HYSYS under the "Column Profiles" of the "Performance" tab. Using the equation above, Excel's Solver program was used to estimate a value for θ . The θ value was substituted into the following equation to find the value of R_{min} . R was then approximated as 1.3 times the R_{min} value. The values of R, R_{min} , and N were then substituted into the Gilliland equation, shown below, to find the actual number of stages in the distillation column. The stage at which the feed enters was calculated using the Kirkbridge equation. The

molar flow rates of the distillate and bottoms, and the K values of the heavy and light key are known.

$$\ln\left(\frac{N_D}{N_B}\right) = 0.206 \cdot \ln\left[\left(\frac{B}{D}\right)\left(\frac{x_{HK}}{x_{LK}}\right)_F \cdot \left(\frac{x_{LK,B}}{x_{HK,D}}\right)^2\right] \quad (5.2.2.2)$$

Moving on to the column internals, a sieve tray was chosen as the type of packing for the following reasons as efficiencies as high as 85% can be achieved, and cost can be minimized. The weir height, tray spacing, and tray efficiency were all assigned industry standard values, as shown in Appendix I.

The tower diameter was chosen based on the flow rates and properties of both the vapor and liquid so as to avoid flooding. The column diameter was then calculated both at the bottom and the top of the column. The vapor and liquid flow rates, as well as the densities at both the first and last trays were found on HYSYS. The fractional downcomer area was then be estimated using the following equation:

$$F_{LG} = \frac{L}{G} \times \left(\frac{\rho_G}{\rho_L}\right)^{0.5} \quad (5.2.2.3)$$

Since the F_{LG} value was less than 0.1, fractional downcomer area was estimated to be 0.1. The tower's inside cross sectional area was calculated as a fraction of the vapor flooding velocity. The fraction, f , was estimated to be 0.8, based on the midpoint of a range of acceptable values. To estimate the vapor flooding velocity, equation 5.2.2.3 was used:

$$U_f = C(\rho_L - \rho_G)^{0.5} \quad \text{where: } C = C_{SB} \cdot F_{ST} \cdot F_F \cdot F_{HA} \quad (5.2.2.4)$$

Each of the parameters were estimated using standard values for sieve tray distillation systems, or in the case of F_{ST} , from plugging the surface tension values, σ , reported by HYSYS into equation 5.2.2.4.

$$F_{ST} = \left(\frac{\sigma}{20}\right)^{0.2} \quad (5.2.2.5)$$

The final equation used to estimate the diameter of the tower, D_T , for both the top and the bottom of the column is given by equation 5.2.2.5.

$$D_T = \left[\frac{4G}{(fU_f)\pi(1-\frac{A_d}{A_r})\rho_G} \right]^{1/2} \quad (5.2.2.6)$$

The column height was estimated using the actual number of trays, along with the standard values for tray spacing, bottom storage and disengagement heights. Since the column diameter calculated in the previous step was within a 6 - 10 ft range, the spacing could be estimated to be 24 inches. As real columns have a lower efficiency due to viscosity effects of the liquid, plate efficiency was determined using the O'Connell correlation. A very approximate estimate of 70% was also used for distillation columns. Multiplying the actual number of trays with the tray spacing and adding the other constant heights gives the overall column height.

Stainless steel was chosen as the material of construction for the downstream distillation column. Stainless steel is comparatively economical to other alloys, and is resistant to corrosion.

In conclusion, the downstream purification of methanol was achieved via a distillation column where the distillate recovered 85% of methanol and the bottoms recovered 91% of the water content. A detailed spreadsheet with the hand calculations for the distillation column is given in Appendix I.

5.2.3 Flash Drum

VL-SEP is a flash drum that separates the raw methanol from the gas components. A horizontal drum is chosen as this process is liquid dominated. The specifications that are required to model this equipment are the residence time, the level of liquid, the position of the inlet stream, and the total height. The residence time was first estimated to be 40s, from a range described in the flash process of Pladis et. al.^[5.2.3.1] The inlet velocity was estimated from the following equation given in a publication from the University of Oklahoma.^[5.2.3.2]

$$u_{max} = 100/\sqrt{\rho_{max}} = 100/\sqrt{31} = 17.96 \text{ m/s} \quad (5.2.3.1)$$

Using the volumetric flow rate of the feed and the u_{max} calculated above, we determined the radius of the feed inlet to be 5.8 inches. The equation for the overall height of the drum was then:

$$L = h_v + h_l + h_f = (36" + r_i) + (12" + r_i) + \frac{V}{\pi \frac{D^2}{4}} \quad (5.2.3.2)$$

The relationship between the diameter and the length of a horizontal flash drum is given by the following relationship.^[5.2.3.3]

$$L = 5D \quad (5.2.3.3)$$

Solving the two equations simultaneously, we determined the length of the drum to be 7.5 m, and the diameter of the drum to be 1.5m.

5.3 Heat Exchangers

5.3.1 Shell and Tube Heat Exchangers

The first part of designing the shell and tube heat exchangers was to determine the LMTD, R, and S values as were calculated below.

$$\begin{aligned}
 LMTD &= \frac{(T_{hot,in} - T_{cold,out}) - (T_{hot,out} - T_{cold,in})}{\ln\left(\frac{T_{hot,in} - T_{cold,out}}{T_{hot,out} - T_{cold,in}}\right)} \\
 &= \frac{(1145 - 400) - (410 - 220)}{\ln\left(\frac{1145 - 400}{410 - 220}\right)} \\
 &= 412.8
 \end{aligned} \tag{5.3.1.1}$$

$$\begin{aligned}
 R &= \frac{T_{hot,in} - T_{hot,out}}{T_{cold,out} - T_{cold,in}} \\
 &= \frac{1165 - 410}{400 - 220} \\
 &= 4.19
 \end{aligned} \tag{5.3.1.2}$$

$$\begin{aligned}
 S &= \frac{T_{cold,out} - T_{cold,in}}{T_{hot,in} - T_{cold,in}} \\
 &= \frac{410 - 220}{1165 - 220} \\
 &= 0.19
 \end{aligned} \tag{5.3.1.3}$$

Using R, S, and figures 12.15 and 12.16 in *Product and Process Design Principles*^[5.3.1.3], the configuration and F_T of the heat exchanger could be determined. This information, the LMTD, the heat duty from the Aspen simulations, and the assumed overall heat transfer coefficient could be used to determine the surface area of heat transfer as seen below.

$$\begin{aligned}
 A &= \frac{Q}{UF_T LMTD} \\
 &= \frac{14800000 BTU/hr}{30 BTU \cdot 0.95 \cdot 412.8} \\
 &= 1261 ft^2
 \end{aligned} \tag{5.3.1.4}$$

The volumetric flow rate of the utilities stream was often found using equation 5.3.1.5 below using physical data from either the Aspen simulation or from *The Engineers Toolbox*^[5.3.1.1, 5.3.1.2].

$$V_{util} = \frac{Q}{\rho C_p \Delta T} \tag{5.3.1.5}$$

$$\begin{aligned}
&= \frac{15700000}{907.5 \frac{\text{kg}}{\text{m}^3} \cdot 4.465 \frac{\text{kJ}}{\text{kgK}} \cdot 100} \\
&= 38.87 \frac{\text{m}^3}{\text{hr}}
\end{aligned}$$

The tube specifications could be found by picking values from Table 12.4 in *Product and Process Design Principles*^[5.3.1.3] and plugging them into equation 5.3.1.6 below until the velocity was found to be between 1 and 10 ft/s. Then the surface area per tube and the number of tubes could be solved.

$$\begin{aligned}
v &= \frac{V_{\text{tube}}}{\frac{A_{\text{sectional}}}{1550} \cdot N} \\
&= \left(\frac{38.87 \frac{\text{m}^3}{\text{hr}}}{\frac{0.182}{1550} \cdot 201} \right) \cdot \frac{\text{ft/s}}{1097.28 \text{ m/s}} \\
&= 1.503 \text{ ft/s}
\end{aligned} \tag{5.3.1.6}$$

$$\begin{aligned}
A_{\text{surface/tube}} &= \frac{O.D. \cdot \pi \cdot L}{12} \\
&= \frac{0.75 \text{ in} \cdot \pi \cdot 16 \text{ ft}}{12 \frac{\text{in}}{\text{ft}}} \\
&= 3.14
\end{aligned} \tag{5.3.1.7}$$

$$\begin{aligned}
N &= \frac{A}{2A_{\text{surface/tube}}} \\
&= \frac{1261 \text{ ft}^2}{2 \cdot 3.14 \text{ ft}^2} \\
&= 201 \text{ tubes}
\end{aligned} \tag{5.3.1.8}$$

Tube length and tube spacing could then be chosen. 16 ft and 1 in, respectively are standard values, however different values may be chosen in order to make the design work. Table 12.6 in *Product and Process Design Principles*^[5.3.1.3] could be used to find the remaining information required. The ratio between the tube length and shell inner diameter could then be checked, with values between five and ten suggesting a good design.

$$\begin{aligned}
\text{Tube } L: \text{ Shell ID} &= \frac{L \cdot 12 \frac{\text{in}}{\text{ft}}}{\text{Shell ID}} \\
&= \frac{16 \text{ ft} \cdot 12 \frac{\text{in}}{\text{ft}}}{25 \text{ in}} \\
&= 7.68
\end{aligned} \tag{5.3.1.9}$$

Once the design passed the two checks, the baffle specifications could be calculated as below.

$$\begin{aligned}
 \text{Baffle Spacing} &= \text{Shell ID} \cdot 0.25 & (5.3.1.10) \\
 &= 25\text{in} \cdot 0.25 \\
 &= 6.25\text{in}
 \end{aligned}$$

$$\begin{aligned}
 \text{Baffle Cut} &= \text{Shell ID} \cdot 0.3 & (5.3.1.11) \\
 &= 25\text{in} \cdot 0.3 \\
 &= 7.5\text{in}
 \end{aligned}$$

$$\begin{aligned}
 \text{Baffle Height} &= \text{Shell ID} - \text{Baffle Cut} & (5.3.1.12) \\
 &= 25\text{in} - 7.5\text{in} \\
 &= 17.5\text{in}
 \end{aligned}$$

Table 5.3.1.1 Heat Exchanger Design Specifications

	Heat 1	Heat 2	Heat 3	Heat 4	Condenser	Reboiler
Utilities	Combustion gas	Low Pressure Steam Generating Water	Low Pressure Steam Generating Water	Low Pressure Steam Generating Water	Cooling Water	Hot Water
Tube Fluid	Stream	Utility	Utility	Stream	Stream	Utility
Tube Flow rate ($\frac{m^3}{hr}$)	2920	38.87	61.17	4464	1904	6297
Tube Inlet T (F)	1500	220	220	788.83	182.8	200
Tube Outlet T (F)	1230	400	450	518	159.6	180
Shell Fluid	Utility	Stream	Stream	Utility	Utility	Stream
Shell Flow rate ($\frac{m^3}{hr}$)	88.38	28810	6064	107	1074	131.4
Shell Inlet T (F)	410	1165	543.2	220	50	165
Shell Outlet T	1202	410	518	450	90	172.3

(F)						
Heat Duty ($\frac{BTU}{hr}$)	$7.835 \cdot 10^7$	$1.575 \cdot 10^7$	$3.550 \cdot 10^6$	$5.498 \cdot 10^7$	$9.972 \cdot 10^7$	$1.038 \cdot 10^8$
Heat Transfer Area (ft^2)	5900	1261	652	3540	18790	102600
Configur-a tion	2-4	2-4	1-2	1-2	1-2	1-2
Shell Diameter (in)	25	25	25	15.25	25	25
Cross Sectional Area (in^2)	1.04	0.182	0.335	1.54	0.334	0.334
Number of Tubes	564	201	78	451	2991	16335
Tube Length (ft)	16	16	16	10	16	16
Tube ID (in)	1.15	0.418	0.67	1.4	0.652	0.652
Tube Gauge (in)	1.25	0.75	1.00	1.50	0.75	0.75
Tube Geometry	Triangle	Triangle	Triangle	Triangle	Triangle	Triangle
Tube Spacing (in)	1	1	1	1	1	1
Tube velocity ($\frac{ft}{s}$)	7.04	1.50	3.31	9.08	2.69	1.63
Baffle	6.25	6.25	6.25	3.8125	6.25	6.25

Spacing (in)						
Baffle Cut (in)	7.5	7.5	7.5	4.575	7.5	7.5
Baffle Height (in)	17.5	17.5	17.5	10.675	17.5	17.5
Overall Heat Transfer Coefficient (BTU)	25	30	30	50	50	50
Materials	316L Stainless Steel	316L Stainless Steel	316L Stainless Steel	316L Stainless Steel	316L Stainless Steel	316L Stainless Steel
Pressure Drop (psi)	3	3	3	3	1.5	1.5

Further calculations can be found and referenced in Appendix J.

5.3.2 Spray Quench

The general method for designing the spray quench is to take the sum of the volumetric flows and multiply them by the assumed time spent in the quench to get the volume of the quench.

$$Volume = time \cdot \Sigma V \quad (5.3.2.1)$$

$$Volume = 10 \text{ sec} \cdot \frac{1 \text{ hr}}{3600 \text{ sec}} \cdot (58.42 + 15251.2) \frac{m^3}{hr}$$

$$Volume = 42.5 m^3$$

Further calculations can be found and referenced in Appendix J.

5.4 Pumps and Compressors

5.4.1 Pumps

Pumps could be modeled by using the pressure difference, capacity and a pump curve among other things. The pressure difference in psi and head ft could be found either by using Bernoulli's equation or by using heuristics. Heuristics were chosen for the calculations as they were often simpler to use. An example of these calculations is provided below.

$$\begin{aligned}
P_{loss, length} &= \frac{2 \cdot L(m) \cdot 3.281 \frac{ft}{m}}{100 \frac{ft}{psi}} \\
&= \frac{2 \cdot 20m \cdot 3.281 \frac{ft}{m}}{100 \frac{ft}{psi}} \\
&= 1.3124psi
\end{aligned} \tag{5.4.1.1}$$

$$\begin{aligned}
P_{loss, height} &= \frac{4 \cdot H(m) \cdot 3.281 \frac{ft}{m}}{10 \frac{ft}{psi}} \\
&= \frac{4 \cdot 10.1m \cdot 3.281 \frac{ft}{m}}{100 \frac{ft}{psi}} \\
&= 13.25524psi
\end{aligned} \tag{5.4.1.2}$$

$$\begin{aligned}
P_{loss, CV} &= CV(valves) * 10 \frac{psi}{valve} \\
&= 2 valves * 10 \frac{psi}{valve} \\
&= 20psi
\end{aligned} \tag{5.4.1.3}$$

$$\begin{aligned}
\Delta P &= P_{reactor} - P_{initial} + P_{loss, length} + P_{loss, height} + P_{loss, control valves} \\
&= 30.40psi - 19.16psi + 1.31psi + 236.23psi + 20psi \\
&= 45.80307441 psi \\
&= 105.805 ft
\end{aligned} \tag{5.4.1.4}$$

The next step was to find the volumetric flow rate in gallons per minute. This could be done with the molar flow rate, molecular weight and density of the stream to be pumped. This information came from the Aspen simulations.

$$\begin{aligned}
V &= Q(\frac{kmol}{hr}) \cdot MW(\frac{kg}{kmol}) \cdot \rho(\frac{kg}{m^3}) \\
&= 662.2(\frac{kmol}{hr}) \cdot 31.9(\frac{kg}{kmol}) \cdot 792.1(\frac{kg}{m^3}) \\
&= 26.669 \frac{m^3}{hr} \\
&= 117.34 gpm
\end{aligned} \tag{5.4.1.5}$$

Now that the pressure and feet have been calculated, pump curves from Fristam pumps^[5.4.1.1] could be used to determine how many pumps were needed in parallel and in series, the impeller diameter, the horse power, theoretical horsepower, NPSHa, and NPSHr. The pump model chosen in this case was the FPR 751 as it was made for handling smaller capacities. This pump operated at 1750 rpm with an inlet diameter of 3 in and an outlet diameter of 2 in.

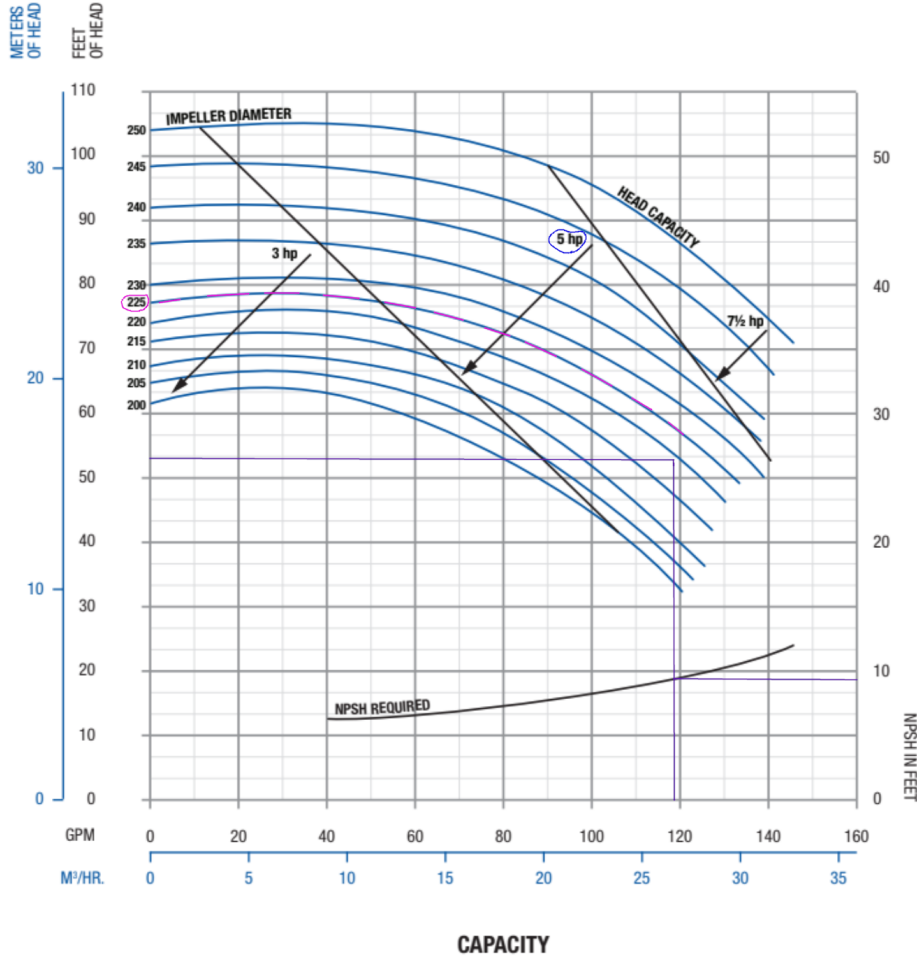


Figure 5.4.1.1 Fristam FPR 751 Pump Curve

When looking at the pressure required and what the pump could handle, it was determined that two pumps in series should be used. The ideal impeller size was determined to be 225 mm, chosen to be the line above the line closest to the location of the pump on the graph just in case any extra pressure is needed. The BHp was determined to be 5Hp as the pump was in the 5Hp range as seen in the graph. To determine the efficiency the BHp needed to be standardized to the inlet stream and compared to the theoretical horsepower.

$$\begin{aligned}
 BHp_{stream} &= BHp_{water} \frac{\rho_{stream}}{\rho_{water}} \\
 &= 5Hp \frac{792.1 \frac{kg}{m^3}}{997.07 \frac{kg}{m^3}} \\
 &= 3.972Hp
 \end{aligned}
 \tag{5.4.1.6}$$

$$THp = \frac{V \Delta P}{\text{Parallel pumps} \cdot \text{Series pumps} \cdot 1714}
 \tag{5.4.1.7}$$

$$= \frac{45.80 \text{ psi} \cdot 117.34 \text{ gpm}}{1.2 \cdot 1714}$$

$$= 1.57 \text{ Hp}$$

$$\eta = \frac{THp}{BHp_{stream}} * 100\% \quad (5.4.1.8)$$

$$= \frac{1.57 \text{ Hp}}{3.972 \text{ Hp}} * 100\%$$

$$= 39.47\%$$

NPSHr could be determined from the pump curve, and in this case it was found to be 9 feet.
NPSHa could be determined from the process below using the initial pressure and vapor pressure from the stream found in the Aspen simulation.

$$NPSHa = P_{initial} - P^* \quad (5.4.1.9)$$

$$NPSHa = (19.16 \text{ psi} - 14.19 \text{ psi}) * \frac{2.31 \text{ ft}}{\text{psi}}$$

$$NPSHa = 11.49 \text{ ft}$$

$NPSHa > NPSHr$ meaning that cavitation should not be a problem.

Table 5.4.1.1 Pump Design Specifications

Parameter	Pump H2O-1	Pump H2O-2	P-100
Pump Type	Centrifugal	Centrifugal	Centrifugal
# in Series	10	10	2
# in Parallel	1	1	1
Capacity (gpm)	94.37	256.89	117.34
Head (ft)	1749.47	1209.83	105.81
Model# and Company	FPR 1161 - Fristam Pumps	FP/FPX 1151 - Fristam Pumps	FPR 751 - Fristam Pumps
RPM (rpm)	1750	1750	1750
Inlet diameter (in)	4	4	3
Outlet diameter (in)	4	4	2
Impeller diameter (mm)	320	275	225

Horsepower (Hp)	20	15	5
Duty (Hp)	20	15	3.97
Theoretical horsepower (Hp)	4.17	7.85	1.57
Efficiency (%)	20.85	52.33	39.47
NPSHa (ft)	32.89	32.89	11.49
NPSHr (ft)	1.5	3.5	9
Material	316L Stainless Steel	316L Stainless Steel	316 Stainless Steel

Further calculations and pump curves can be found in Appendix K.

5.4.2 Compressors

For the compressor it was required to find the pressure ratio, the corrected mass flow rate and the outlet temperature. This could be done using values from our Aspen simulation and equation 5.4.2.2 which came from Turbonetics^[5.4.2.2]

$$\begin{aligned}\frac{P_F}{P_I} &= \frac{80bar}{35bar} \\ &= 2.29\end{aligned}\tag{5.4.2.1}$$

$$\begin{aligned}Corrected\ Mass\ Flow &= Mass\ Flow \cdot \sqrt{\frac{T_I}{545} / \frac{P_I}{28.4}} \\ &= 5076.29 \frac{lb}{min} \cdot \sqrt{\frac{285.44\ F}{545} / \frac{507.63psi}{28.4}} \\ &= 205.5\ lb/min\end{aligned}\tag{5.4.2.2}$$

Efficiency could be found using the compressor curve obtained from Turbonetics^[5.4.2.2].

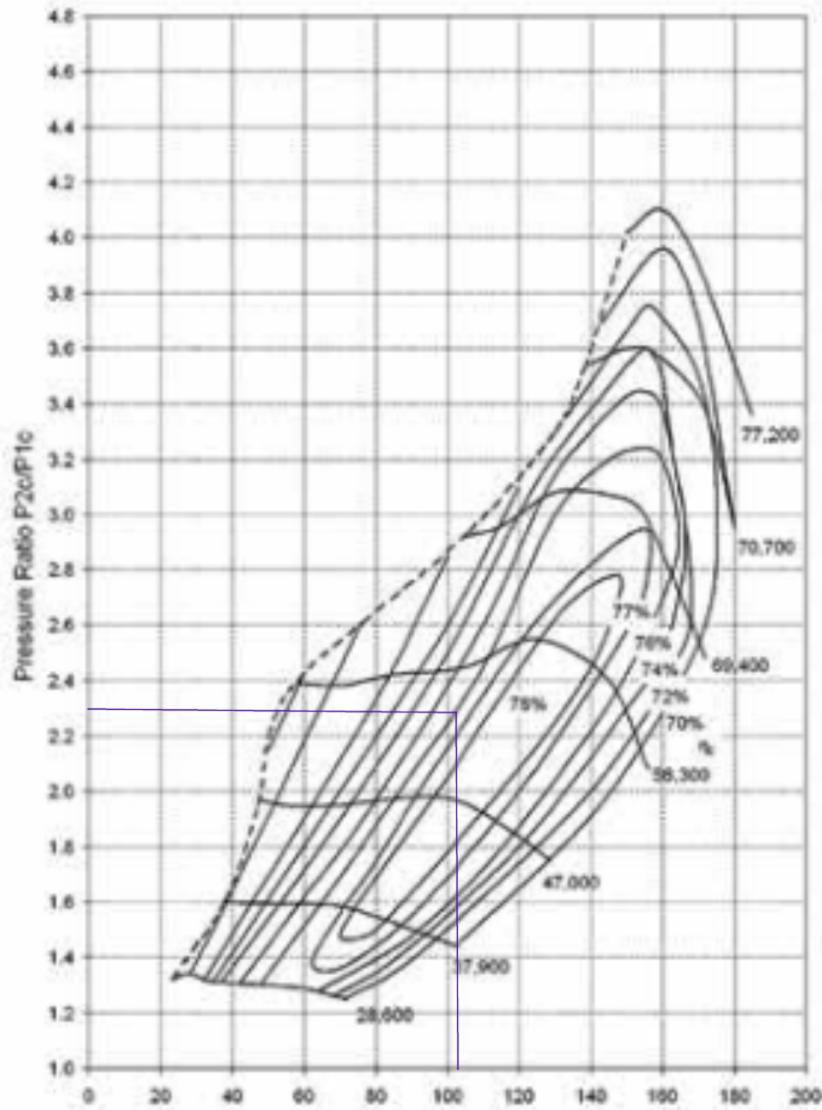


Figure 5.4.2.1 Compressor Efficiency Curve

From the above diagram it could be seen that to be within the brake line and choke line, 2 compressors must be used in parallel to halve the corrected mass air flow for each compressor. Efficiency was determined to be 0.76, or 76%.

The Horsepower per pump could be estimated by rounding the corrected mass flow for each pump multiplied by ten to the tenths place

$$\begin{aligned}
 \text{Horsepower} &= \text{roundup}(\text{CMF}/2 * 10) \\
 &= \text{roundup}(102.75*10) \\
 &= 1000\text{Hp}
 \end{aligned}
 \tag{5.4.2.3}$$

The outlet temperature for an isentropic compression could be determined through the process outlined below using the equation from Moshfeghian (2011)^[5.4.2.1].

$$\begin{aligned}
 T_2 &= T_1 \cdot \left(1 + \frac{\left(\frac{P_F}{P_I}\right)^{(k-1)/k} - 1}{\eta}\right) \\
 &= ((140.8 + 273.15)K \cdot (1 + \frac{(2.29)^{(1.39-1)/1.39} - 1}{0.76}) - 273.15K) \\
 &= 284.0^\circ C
 \end{aligned}
 \tag{5.4.2.4}$$

Table 5.4.2.1 Compressor Design Specifications

	Compressor 1.A	Compressor 1.B
Inlet Pressure (bar)	35	35
Outlet Pressure (bar)	80	80
Pressure Ratio	2.29	2.29
Inlet Temperature (C)	140.8	140.8
Outlet Temperature (C)	284.0	284.0
Corrected Mass Flow (lb/min)	102.75	102.75
Duty (Hp)	1000	1000
Efficiency (%)	76	76
Manufacturer	Turbonetics	Turbonetics

Further calculations can be found in Appendix K.

5.5 Heliostat Design

One more experimental technique for obtaining high temperatures in reactors is through the use of a heliostat field to harness the energy of sunlight. Though currently not in widespread use, heliostats have been considered and even implemented for a variety of research and even industrial applications. The premise of the heliostat is to concentrate energy from the sun through focusing sunlight through a series of prisms, mirrors, or other reflective surfaces to a receiver which will convert that energy into a more usable form— typically turning a generator to produce electricity, or providing heat as in this application. Modeling of this relatively new technology in terms of either technological optimization and economic approximation is complex and still to some degree in development, though largely based upon optics calculations. Accordingly, many simplifications and assumptions were employed in the formation of a design for a heliostat field

intended to supply the solar thermal reactor with sufficient energy to raise its temperature to the required reaction temperature of 1450 °C.

The heliostat design for this methanol synthesis process is based almost entirely on the work of Allan Lewandowski (2022)^[5.5]. The Excel spreadsheets provided by Mr. Lewandowski, which can be referenced in Appendix L, enabled the calculation of tower height and corresponding optimal solar field design based upon the energy requirements of the reactor as modeled in Aspen Plus. A reactor model was created for high (8000x), low (2000x), and intermediate (4000x) concentration designs.

The heat duty of the solar thermal reactor as modeled in Aspen Plus was found to be 174,866 kWh/hr. The problem statement allowed the other necessary inputs to be added. The solar thermal reactor was stated to be operational for 2920 hours each year of operation. As also specified by the problem statement, the solar thermal reactor temperature could be assumed to remain constant at 1450 °C. For simplicity, the nominal fraction from solar was assumed to be one.

The maximum tower height, regardless of the concentration of sunlight being investigated, was 200 m. In determining the height of the towers and the number of towers required, a trial and error process was performed in order to determine the smallest number of towers and the lowest height that would fulfill the energy requirements of the reactor. In addition to the number of towers and tower height, the Excel spreadsheet applied several assumptions in order to model the heliostat and secondary areas associated with each tower. The heliostat dimension was assumed to be 1/20 of the height of the tower, and the heliostats were assumed to be square or at least have an area equal to the dimension squared. A central receiver model was used. Secondary concentrators were also utilized, and the required CPC area was designed within the spreadsheet for a 95% intercept with a single tower and 3 CPC fields at the design point (a tower of 200 m) and then linear scaling was applied in order to calculate the CPC area based upon the tower height determined based on the input conditions. The tower design parameters for each of the three concentration designs are provided below in Table 5.5.1.

Table 5.5.1 Heliostat Parameter Data at 2000, 4000, and 8000 Suns

Concentration	Number of Towers	Tower Height (m)	Heliostat Area (m ²)	Secondary CPC Area (m ²)
2000 x	2	157	668,111	614
4000 x	2	180	453,924	591
8000 x	4	188	379,595	746

In order to decide which of the designs would be best now that a design had been constructed for each solar concentration that would meet the energy requirements of the system, economic analysis was performed. The total cost of the heliostat design was considered to be the sum of the cost of the secondary concentrators, the cost of the heliostats, and the cost of the tower. The expressions for these costs (not taking into account inflation, which can be modeled as a coefficient that would be constant for all three designs) were as follows:

$$\text{Heliostat Cost} = \$125/\text{m}^2 \quad (5.5.1)$$

$$\text{Secondary Area Cost} = \$1,250/\text{m}^2 \quad (5.5.2)$$

$$\text{Tower Cost} = 1.41 * (\$600,000 + 17.72 * (\text{Height in m})^{2.392}) \quad (5.5.3)$$

Using these expressions, the cost for each heliostat design was calculated for comparison in Table 5.5.2.

Table 5.5.2 Comparative Heliostat Design Costs

Concentration	Heliostat Cost	Secondary Cost	Tower Cost (All Towers)	Total Cost
2000 x	\$83,513,875	\$767,500	\$10,631,326	\$94,912,701
4000 x	\$56,740,500	\$738,750	\$14,089,230	\$71,568,480
8000 x	\$47,449,375	\$932,500	\$30,896,395	\$79,278,270

Based upon this economic analysis, the second heliostat model (4000 suns concentration) was the most economically advantageous. As a result, this was the design that was selected for use as part of the methanol production facility. This heliostat field consisted of two central receiver towers, each encircled by three heliostat fields. The towers were 180 meters tall, with a 35° lookout angle and a 35° acceptance angle. Each heliostat had an area of 81 m², and there were 934 heliostats per field for a total area of 75654 m² of heliostats per field. The CPC (compound parabolic concentrator) area was 98.4 m² per field. With two towers and three fields per tower, that resulted in a total of 5604 heliostats, for a total of 453,924 m² of heliostat area and 591 m² of CPC area. The annual efficiency was 0.402, and the heliostat design cost \$71,568,480 for installation and equipment—again, not taking into account inflation from 2006 to 2022.

6 Utilities Summary and Heat Integration

The utilities used for this chemical process were largely the heating and cooling fluids used in the heat exchangers, which had the potential to be significantly reduced by heat integration. There was also an electrical demand, which was not impacted by heat integration and remained constant regardless of the case. Electricity was used for the pumps and compressors in both the downstream and upstream processes, and was calculated based upon the heat duties of the

pumps. 1000 Hp total were required for the compressors, 200 Hp was needed for the pumps responsible for the inlet reacting water stream to the solar thermal reactor, 150 Hp was allocated to the pumps supplying water to the spray quench, and 7.94 Hp was needed for the pump to the downstream distillation column, and was accordingly neglected from this calculation as the utilities summary has only been performed for the upstream process. The calculation of electricity requirements were performed as follows:

$$(1000 + 200 + 150 \text{ Hp}) \left(\frac{0.7457 \text{ kW}}{\text{Hp}} \right) \left(2920 \frac{\text{hrs}}{\text{year}} \right) = 2939549.4 \frac{\text{kWh}}{\text{year}} \quad (6.1)$$

Without heat integration, the water requirement was only the water fed into the solar thermal reactor, which was fed at a rate of 21,402.2 kg per hour. The rest of the utilities were due to the heat exchangers in the system, which were dramatically affected by the presence or absence of heat integration. Three models have been provided for comparison: the heat exchanger reactor design based upon hand calculations (shown in depth in section 5.3.1), a base-case model performed by Aspen Energy Analyzer, and a heat integration model also performed by Aspen Energy Analyzer. The file can be referenced in Appendix M.

The majority of the hand calculated values were taken directly from the heat exchanger design. 88.38 cubic meters per hour of combustion gas were needed, and the spray quench and the heat exchangers were all fed cooling water. A conversion was formed to get the spray quench inflow of water into units of cubic meters per hour, as follows:

$$3234 \frac{\text{kmol}}{\text{hr}} \left(\frac{18.02 \text{ kg}}{\text{kmol}} \right) \left(\frac{1 \text{ m}^3}{10^3 \text{ kg}} \right) = 58.28 \text{ m}^3/\text{hr} \quad (6.2)$$

This value was then added to the inlet flow rates of cooling water for the three heat exchangers experiencing cooling for a total cooling water requirement in all the heat exchangers of 265.31 cubic meters per hour. The spray quench did not produce steam as part of the cooling process, but the heat exchangers did, and the steam production was calculated. This was assumed to be low-pressure steam.

$$(38.86 + 61.17 + 107 \frac{\text{m}^3 \text{ water}}{\text{hr}}) \left(\frac{10^3 \text{ kg}}{\text{m}^3 \text{ water}} \right) \left(\frac{\text{m}^3 \text{ steam}}{0.6 \text{ kg}} \right) = 345,066.67 \text{ m}^3 \text{ steam/hr} \quad (6.3)$$

The Aspen simulation, the creation of which was explained in depth in section 4, was used in order to create an Aspen Energy Analyzer file for use in heat integration. This model specified its own utilities, independent of the hand-calculated heat integration design. The base case arrangement was described by Figure 6.1.

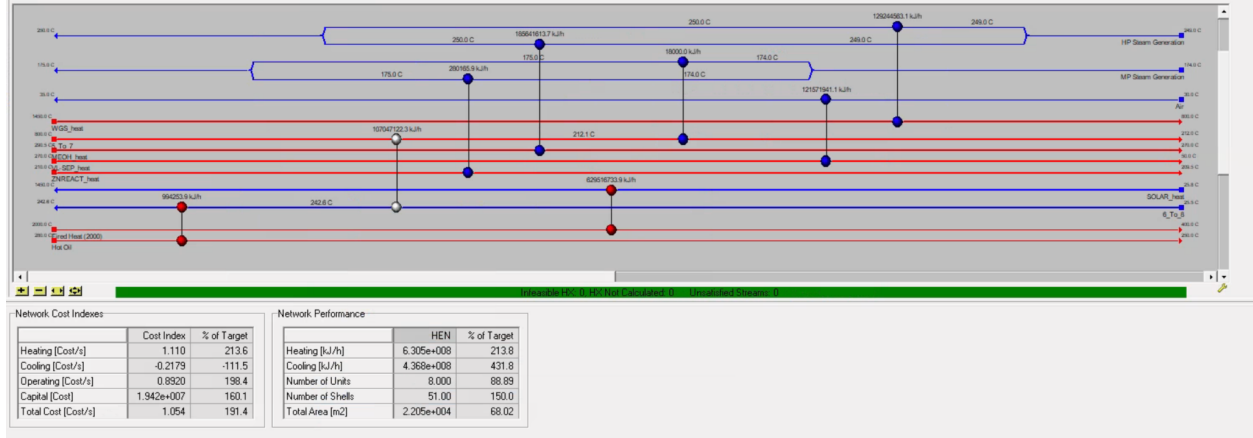


Figure 6.1 Base Case Energy Analyzer Heat Exchanger Model

Precise flow rates were difficult to find for the base-case scenario and tended to be represented as zero even if heat duty was present. Approximate hand calculations were performed for each utility, but the heat duties have been provided for reference as well. In the base case, the heating streams were oil and fired heat, and cooling was provided by air and both medium and high pressure steam generation. The heat duties are listed below as follows:

$$\text{Oil: } 9.94 * 10^5 \frac{\text{kJ}}{\text{hr}} \quad (6.4)$$

$$\text{Fired Heat: } 6.30 * 10^8 \frac{\text{kJ}}{\text{hr}} \quad (6.5)$$

$$\text{Air: } 1.22 * 10^8 \frac{\text{kJ}}{\text{hr}} \quad (6.6)$$

$$\text{MP Steam: } 2.98 * 10^5 \frac{\text{kJ}}{\text{hr}} \quad (6.7)$$

$$\text{HP Steam: } 3.15 * 10^8 \frac{\text{kJ}}{\text{hr}} \quad (6.8)$$

Where possible, conversions were performed to get an approximate mass and then an approximate volumetric flow rate using the expression $Q = mC_p \Delta T$, rearranged as $m = \frac{Q}{C_p \Delta T}$.

For steam generation, the equation was amended to $Q = m(\Delta H_{vap})$ where ΔH_{vap} was assumed to be 2257 kJ/kg, the evaporation energy of water. Heat capacities were approximated as the effective heat capacities of the streams given in Aspen. The change in temperature was read directly from the utility steam. No conversion could be performed for fired heat, as no clearly defined mass or volume could be logically associated with that form of heating.

$$\text{Oil: } \frac{9.94 * 10^5 \frac{\text{kJ}}{\text{hr}}}{3.00 \frac{\text{kJ}}{\text{kg-K}} * (30 \text{ K})} \left(\frac{1 \text{ m}^3}{850 \text{ kg}} \right) = 12.99 \text{ m}^3/\text{hr} \quad (6.9)$$

$$\text{Air: } \frac{1.22 * 10^8 \frac{\text{kJ}}{\text{hr}}}{1.00 \frac{\text{kJ}}{\text{kg-K}} * (5 \text{ K})} \left(\frac{1 \text{ m}^3}{1.225 \text{ kg}} \right) = 19,918,367.35 \text{ m}^3/\text{hr} \quad (6.10)$$

$$MP\ Steam: \frac{2.98 \cdot 10^5 \frac{kJ}{hr}}{2257 \frac{kJ}{kg}} \left(\frac{1 m^3}{0.6 kg} \right) = 220.06 m^3/hr \quad (6.11)$$

$$MP\ Steam: \frac{3.15 \cdot 10^8 \frac{kJ}{hr}}{2257 \frac{kJ}{kg}} \left(\frac{1 m^3}{0.6 kg} \right) = 232,609.66 m^3/hr \quad (6.12)$$

From the generated steam, the water utility required could be calculated.

$$(232,609.66 + 220.06 \frac{m^3\ steam}{hr}) \left(\frac{0.6 kg\ H_2O}{m^3\ steam} \right) \left(\frac{1 m^3\ water}{10^3 kg\ H_2O} \right) = 139.70 m^3/hr \quad (6.13)$$

Using Aspen Energy Analyzer, three heat integrated cases were created for consideration and the best one was selected. These aimed to optimize heat transfer between process streams to minimize the amount of utilities required to obtain the necessary heat exchange in the process system. Of the three, one of the models could not be induced to converge regardless of retrofitting, and that model was accordingly discounted from further consideration. For the remaining two models, Table 6.1 has been provided comparing key elements of the heat integration design.

Table 6.1 Heat Integration Model Comparison

Design	Design A	Design B
Number of Heat Exchangers	15	12
Percent of Required Heating Provided	100.7%	134.0%
Percent of Required Cooling Provided	102.0%	102.0%
Heating Utility	Fired Heat	Fired Heat
Cooling Utility	MP Steam Generation	MP Steam Generation

The same utilities were used in both cases, and the same cooling percentage was obtained. This suggested that there would be no benefit for either design in terms of the ability to sell the steam produced by heating for an economic credit. The primary difference between the cases was the number of heat exchangers and the percentage of heating provided by the utilities. Economically, it would be preferable to minimize the number of heat exchangers and obtain heating and cooling near 100% of the requirement so that unnecessary utilities will not be used. Waste heat in particular can provide an environmental as well as economic challenge, and should be minimized where possible. Heat exchangers present a one-time cost, while excess utility used presents a continuous cost. Accordingly, design A was selected as the heat integrated design for use. The

Aspen Energy Analyzer model of the heat-integrated network of heat exchangers was presented in Figure 6.2.

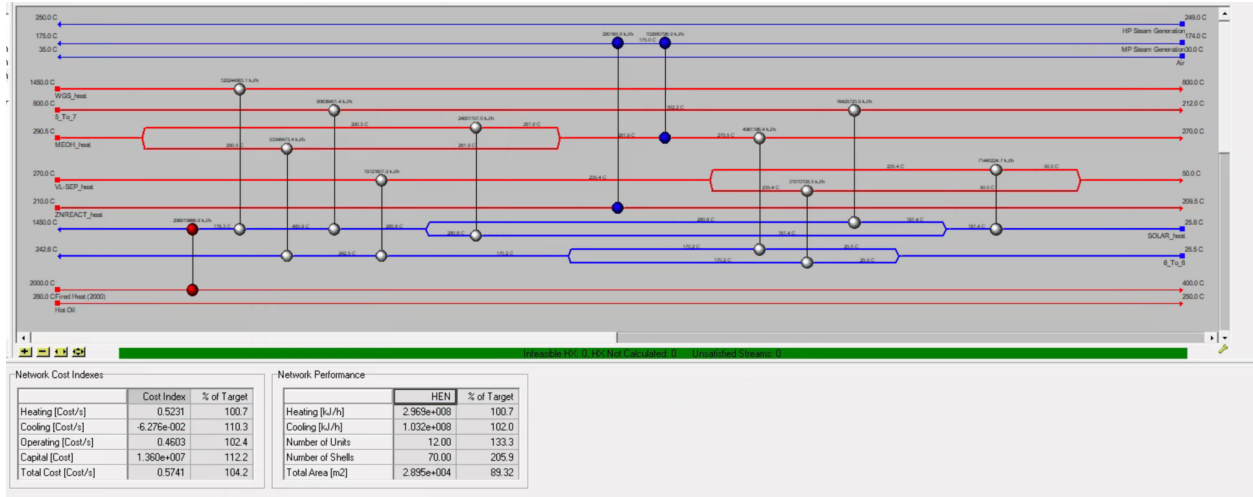


Figure 6.2 Heat Integrated Energy Analyzer Model

For the heat integrated case, the flow rates could directly be pulled from the simulation. Fired heat was provided at a reported rate of 1.856×10^5 kg/hr, but as mentioned earlier the physical significance of this weight was not clear and the reporting of the requirement of fired heat was accordingly done based upon the heat duty of the stream. In addition, the flowrate of medium-pressure (MP) steam was also read directly from the heat integration simulation model, and was given as 5.206×10^4 kg/hr of steam. As before, this mass flow rate could be converted into a volumetric flowrate and could also be used to calculate the required cooling water utility to be fed.

$$5.206 \times 10^4 \frac{\text{kg}}{\text{hr}} \left(\frac{1 \text{ m}^3 \text{ steam}}{0.6 \text{ kg}} \right) = 86,766.67 \frac{\text{m}^3}{\text{hr}} \quad (6.14)$$

$$86,766.67 \frac{\text{m}^3 \text{ steam}}{\text{hr}} \left(\frac{0.6 \text{ kg H}_2\text{O}}{\text{m}^3 \text{ steam}} \right) \left(\frac{1 \text{ m}^3 \text{ water}}{10^3 \text{ kg H}_2\text{O}} \right) = 52.06 \frac{\text{m}^3 \text{ H}_2\text{O}}{\text{hr}} \quad (6.15)$$

The heat duties for the two utilities streams were expressed below. A summary of the heat exchanger utilities in all three cases was provided in Table 6.2.

$$\text{Fired Heat: } 2.97 \times 10^8 \frac{\text{kJ}}{\text{hr}} \quad (6.16)$$

$$\text{MP Steam: } 1.03 \times 10^8 \frac{\text{kJ}}{\text{hr}} \quad (6.17)$$

Table 6.2 Utilities Summary

Utility	Hand Calculated Heat Exchangers	Aspen Base Case	Aspen with Heat Integration
Number of Heat Exchangers	5	8	15
Combustion Gas	88.38 m ³ /hr	--	--
Cooling Water*	265.31 m ³ /hr	139.70 m ³ /hr	52.06 m ³ /hr
Steam Generation (LP)	345,066.67 m ³ /hr	--	--
Oil	--	12.99 m ³ /hr	--
Fired Heat	--	6.30 * 10 ⁸ kJ/hr	2.97 * 10 ⁸ kJ/hr
Air	--	19,918,367.35 m ³ /hr	--
Steam Generation (MP)	--	220.06 m ³ /hr	86,766.67 m ³ /hr
Steam Generation (HP)	--	232,609.66 m ³ /hr	--

* This value does not include the process water fed into the solar thermal reactor for any of the three cases.

The heat integration case drastically reduced the number of utilities needed, particularly compared to the Aspen base case. While more heat exchangers were needed, it was reasonable to assume that those would likely be on a smaller scale than those needed based on the hand calculations. While economic optimization would need to be performed to truly understand how each case compared, it would be reasonable to assume that the heat integrated case would likely prove to be the more economical design as well as the more environmentally preferable design by reducing the amount of utilities required and avoiding waste heat by using process streams as heat transfer fluid options.

7 Estimation of Capital Investment, Cash Flow, and Profitability Analysis

Implementation of this system is not solely reliant upon technical design and possibility, but also on economic viability. A profitability analysis study was performed on the methanol production process discussed at length in this report. Capital and variable costs were the key costs that were calculated in depth, and will be discussed in the following sections. The site used for this model was the US West Coast. Inflation was taken to be 4% throughout. The majority of the equipment occurred in the upstream process, and so the target amount of product (56 million gallons of pure

methanol) was divided by the number of operating hours per year in the upstream process only. When the downstream distillation process was addressed, a conversion in operational time had to be performed. The Weimer Project Economics file, with five-year MACR depreciation, was utilized for all economic calculations^[7.5].

7.1 Capital Cost

Capital costs primarily consisted of the costs of purchase, delivery, and installation of the various pieces of equipment required for the processing of biomass into syngas and the subsequent conversion of the syngas into methanol and the purification of the methanol stream to the final product. The bare module method was used, though comparison to the Lang Factor approach was also applied as a check on the order of magnitude of the capital cost estimation as established in this section. Each of the key pieces of equipment were priced individually, as explained as follows. Miscellaneous equipment was assumed to add an additional ten percent of the equipment cost, to account for equipment that was not explicitly calculated for. In addition to the equipment, site factors were also taken into account: as this was a new project, the cost of site preparation accounted for a 15% increase on the sum of all principle costs of equipment with FBM multiplicative factors accounted for, with another 20% for the cost of service facilities.

Heliostat Towers and Field

As explained in section 5.5, the final design of the heliostat field and tower requirements for the solar thermal reactor consisted of two 180 meter towers, with a total of 453,924 square meters of heliostats and 591 square meters of secondary concentrators. The FBM factor for all three of these components was assumed to be one. The tower pricing model (7.1.1) was created in 2008, so that a conversion had to be applied using the CE indexes for 2022 and 2008 to account for inflation. The CE index for 2022 was assumed to be 831, while that for 2008 was found to be 575.4. Both the heliostat (7.1.2) and secondary concentrator pricing equations (7.1.3) were accurate to 2022 and no conversion had to be applied for inflation in those cases. All prices were put in terms of thousands of dollars for use in the economics Excel file.

$$\text{Heliostats} = \$125 / m^2 * (453,924 m^2) = \$56,740.50k \quad (7.1.1)$$

$$\text{Secondary Concentrators} = \$1250 / m^2 * (591 m^2) = \$738.75k \quad (7.1.2)$$

$$\text{Tower} = [\$600,000 + 17.72(180 m)^{2.392}] * 1.41 * \frac{831}{575.4} = \$10,173.92k \quad (7.1.3)$$

With two towers, the total price of the heliostat field was found to be \$77,827.10k.

Solar Thermal Reactor

The solar thermal reactor was approximated as the sum of the silicon carbide tubes contained within the reactor and an outer stainless steel tank. The cost for the silicon carbide tubes was given in the problem statement, but the tank cost (like the components with the exception of the distillation column) was found on Matche and a conversion was performed between the 2022 CE index and the CE index for 2014, which was 576.1. The FBM factor was 4.3, which was typical for a reactor as found in Table 16.14 of the textbook for the course^[7.4].

$$SiC\ Cost = 3\ tubes * (\frac{\$2500}{ft})(25m)(\frac{3.28\ ft}{m}) = \$615k \quad (7.1.4)$$

The outer tank was defined in Matche as a ‘Vertical, shop fab, small’ stainless steel tank with a volume of 1651 gallons (6.25 cubic meters)^[7.2].

$$Tank\ Cost = \$48,900 * \frac{831}{576.1} = \$70.54k \quad (7.1.5)$$

The total PE cost of the solar thermal reactor was found to be \$685.54k.

Zinc Oxide Reactor

The zinc oxide bed reactor was modeled economically as a horizontal tube with a volume of 4200 L (1110 gallons). It was filled with solid zinc oxide pellets, which constituted a large portion of the cost of this part of the process. However, the solid zinc oxide was classified as a variable cost, as the pellets needed to be refreshed. In order to refresh them, two zinc oxide beds were needed to meet the operating time requirement of this reactor. That way, one could be replenished while the other was in use. Horizontal pressure vessels typically can be represented with an FBM factor of 3.05^[7.4]. Price estimation was performed using a horizontal stainless steel tank with rounded ends and a volume of 1110 gallons^[7.2].

$$ZnO\ Reactor = 2 * \$18,000 * \frac{831}{576.1} = \$52.93k \quad (7.1.6)$$

Methanol Reactor

The methanol reactor was modeled as a shell-and-tube heat exchanger, with the cost multiplied by four to account for the additional complexity of the reactor compared to an average heat exchanger. The heat transfer area of all the tubes present (number of tubes multiplied by the surface area of each tube) was found to be 70,428 square feet. Similarly to the zinc oxide reactor, a FBM factor of 4.3 was used to account for the complexity of installation of the reactor rather than an ordinary heat exchanger. The large stainless steel shell-and-tube fixed/U steel heat exchanger cost \$1,346,400 in 2014^[7.2].

$$MeOH\ Reactor = 4 * \$1,346,400 * \frac{831}{576.1} = \$7,768.50k \quad (7.1.7)$$

Cyclones

As explained in section 5.2.1, two cyclones were required. Both had an FBM of 2.15 when modeled in Excel, as they were assumed to be similar to a compressor/driver^[7.4]. The main cyclone had a diameter of 2.25 meters (88.58 inches), while the component labeled Zn-Split had a diameter of 6.5 meters (255.91 inches). Both cyclones were priced in Matche as air sweep dry cyclones, the only cyclone present on the site that had a diameter range of similar size to those calculated during the design phase of this investigation.

$$\text{Cyclone Cost} = (\$112,000 + \$307,200) * \frac{831}{576.1} = \$604.68k \quad (7.1.8)$$

Heat Exchangers

Several shell and tube heat exchangers were present in the final system design. In addition, there was also a compressor and a reboiler present on the primary distillation column used to process and purify the final methanol product. Each heat exchanger was assumed to be stainless steel, and an FMB factor of 3.17 was used as was standard for heat exchangers^[7.4]. The individual prices of the heat exchangers have been provided below, in Table 7.1.1. As above, the heat transfer area was calculated by multiplying the theoretical number of tubes by the theoretical surface area of each individual tube.

Table 7.1.1 Heat Exchanger Pricing

Heat Exchanger	Heat Transfer Area (ft ²)	Matche Heat Exchanger Used	Price in 2014 ^[7.2]
Heat 1	2,950.20	Shell/Tube, Fixed/U, Large	\$306k
Heat 2	630.33	Shell/Tube, Fixed/U, Medium	\$96.10k
Heat 3	326.08	Shell/Tube, Fixed/U, Medium	\$50.50k
Heat 4	1770.13	Shell/Tube, Fixed/U, Large	\$241k
Reboiler	51,322.00	Reboiler	\$4107.80k
Condenser	9395.79	Condenser	\$801.80k

The total price of the heat exchangers was \$5,603.20k in 2014, which converted to \$8,082.38k in 2022.

Spray Quench

The spray quench was treated economically as being similar to a shell-and-tube heat exchanger with twice the pricing due to additional complexity. The same FBM factor of 3.17 was used as for the other, shell-and-tube, heat exchangers. The heat transfer area was calculated as 45.59

square feet, and the spray quench was rated for the highest possible pressure option in Matche, 900 psi (62 bar). The price of the spray quench was accordingly calculated using the following equation, 7.1.9.

$$\text{Spray Quench} = \$47,200 * 2 * \frac{831}{576.1} = \$136.17k \quad (7.1.9)$$

Storage Tanks

Tanks were assumed to be low complexity to install, and were designated with an FBM factor of 1.73, equivalent to screens^[7.4]. It was assumed that, since the downstream methanol processing plant was operational more than the upstream production plant theoretically transportation time between the sites would be limited, storage for a week's worth of methanol production at the upstream plant would be sufficient in terms of general storage needs. With 19,178 gallons produced per operational hour, a week's worth of methanol production was calculated as follows:

$$19178 \frac{\text{gallons}}{\text{hr}} \left(\frac{8 \text{ operational hours}}{\text{day}} \right) \left(\frac{7 \text{ days}}{\text{week}} \right) (1 \text{ week}) = 1,073,968 \text{ gallons} \quad (7.1.10)$$

The largest reasonable volume tank on Matche was found to be the API, Cone Roof, Field Fab tank, made of stainless steel^[7.2]. A brief optimization was performed as in Table 7.1.2. in order to establish the best combination of size and tank number to acquire near the required storage capacity.

Table 7.1.2 Storage Tank Price Optimization

Tank Size (Gallons)	Number of Tanks Needed	Total Cost for All Tanks (2014)
200,000	6	\$2,089.80k
400,000	3	\$1,488.00k
600,000	2	\$1,219.80k
800,000	2	\$1,412.60k
1,000,000	1	\$791.40k

It was found that fewer larger tanks was economically preferable, so the largest tank size was selected and used. Correcting for inflation between 2014 and 2022, the total cost of the storage tank was found to be \$1,141.56k.

Pumps

Several pumps were needed throughout the process. The FBM for the pumps was 3.3^[7.4]. All the pumps used in this system were centrifugal pumps arranged in series, and all were sized as

‘inline, API-610 w/ motor, 316 stainless steel, packing’ in Matche^[7.2]. The three different sets of pumps in series differed in cost based upon their outlet diameters and the heads (in feet) provided. A summary of the prices for the pumps was given in Table 7.1.3.

Table 7.1.3 Pricing of the Process Centrifugal Pumps

Pump Section	Pump H2O-1	Pump H2O-2	P-100
Number of Pumps in Series	10	10	2
Required Head (Total) (ft)	1749	1209	106
Required Head per pump (ft)	175	121	11
Matche Pump Head (ft)	400	150	150
Outlet Diameter (in)	4	4	2
Cost in 2014 per pump [7.2]	\$57,700	\$31,600	\$23,000
Cost in 2014 for all pumps	\$577k	\$316k	\$46k

Overall, the total price for all the centrifugal pumps in 2022 was calculated:

$$Pumps = \$939k * \frac{831}{576.1} = \$1,354.47k \quad (7.1.11)$$

Compressors

Two identical compressors were used, both with the standard FBM factor of 2.15 for compressors. In Matche, the compressors were selected for the sake of economics to be centrifugal compressors rated for the highest offered pressure of 1000 bar, and capable of supplying the required 2060 Hp. The Matche compressors were only available in carbon steel, and so an additional factor had to be applied in order to obtain an approximation for cost of the compressors if they had been composed of stainless steel.

$$Compressors = 2 * \$887,100 * \frac{831}{576.1} * \frac{2.00 (SS)}{1.00 (CS)} = \$5,118.42k \quad (7.1.12)$$

Distillation Columns and Flash Drums

Two separation columns, the one required for the methanol purification and the one labeled VL-Sep, were present in the process. As opposed to the rest of the economic approximations of the components, the distillation columns were priced according to the Peters and Timmerhaus (2001) Cost Formulas Excel file. Both were assumed to be stainless steel, with a FBM factor of 4.16^[7.4]. The methanol purification column had a maximum pressure of 46 psi (317 kPa)-- which was deemed to imply no pressure rating as this value was much lower than the pressures for the distillation columns rated for high pressure-- a diameter of 11 feet (3.35 meters), and a height of 104.43 feet. From the Cost Formulas file, the expression for calculating cost would be described by equation 7.1.13 with height, x , in meters^[7.3]. The coefficients have been truncated here for brevity.

$$Price = -19.1047x^2 + 19291.7520x + 93308.1455 = \$1899.60k \quad (7.1.13)$$

The VL-Sep is a flash separator that will be modeled as a column with no trays. It had a similar pressure drop, so again there was no pressure rating involved. The column had a diameter of 1.5 meters, and a height of 20 ft (6.096 m). Since there was not a diameter option in the spreadsheet that matched that of the column, interpolation was performed between the cost of the distillation column with a 1 meter diameter and a 2 meter diameter.

$$Price_{1\text{ meter}} = 53.5181x^2 + 7793.5451x + 7110.4000 = \$56.61k \quad (7.1.14)$$

$$Price_{2\text{ meter}} = 11.5689x^2 + 12062.2439x + 27537.1414 = \$101.50k \quad (7.1.15)$$

By interpolation the price of the tower with 1.5 meters diameter was \$79.06k. Taking into account inflation, the CE Index used for the file was 500 and the CE index for 2022 was again 831, such that the total price of both of the separation columns was \$3288.53k.

Fixed Capital Investment

With all the principal equipment costs and FBM factors taken into account, the cost of all equipment purchased and delivered was found to be \$190,102k. With site costs and inflation also included under fixed capital investment the total depreciable capital, or fixed capital investment, was calculated as being \$1,091,500k. By the Lang Factor method, the fixed capital investment for a solid-fluids processing plant was approximated to be \$499,327k, about half the value calculated using the bare module cost method. This discrepancy was assumed to be due to the complexity of installation and site factors (including building the plant on the US West Coast), that were not taken into account by the Lang Factor method.

7.2 Working Capital

The working capital was assumed to be 2.5% of the total depreciable capital/ fixed capital investment. The fixed capital cost as described in section 7.1 came to \$190,102k, such that the working capital represented an additional \$27,288k.

7.3 Variable Cost

The ingredients and utilities were scaled such that a cost per gallon of methanol produced could be calculated. Reactants, utilities, and additional catalysts and cooling fluid chemicals were all calculated, and a carbon credit was experimentally derived in order for the methanol cost per gallon to be calculated to the desired value of 1.76 dollars per gallon.

Reactants

The biomass price was provided as \$80 per ton of biomass. Using the Aspen Plus inlet flow rate of biomass, the tons of biomass per gallon of methanol were calculated.

$$192.73 \frac{\text{kmol biomass}}{\text{hr}} \left(\frac{133.60 \text{ g}}{\text{mol biomass}} \right) \left(\frac{1000 \text{ mol}}{\text{kmol}} \right) \left(\frac{1 \text{ ton}}{10^6 \text{ g}} \right) = 25.75 \text{ ton/hr} \quad (7.3.1)$$

$$\frac{25.75 \text{ ton/hr}}{19178 \text{ gal/min}} = 0.001343 \text{ tons per gallon} \quad (7.3.2)$$

Methane was provided at a price of \$0.005 per standard cubic foot.

$$848.1 \frac{\text{kmol methane}}{\text{hr}} \left(\frac{1000 \text{ mol}}{\text{kmol}} \right) \left(\frac{1 \text{ SCF}}{1.1956 \text{ mol}} \right) \left(\frac{1}{19178 \text{ gal/hr}} \right) = 36.98 \text{ SCF/gal} \quad (7.3.3)$$

Zinc oxide cost \$0.25 per kg.

$$\frac{191.50 \text{ kg ZnO/hr}}{19178 \text{ gal/hr}} = 0.009985 \text{ kg/gal} \quad (7.3.4)$$

Catalysts and Chemicals

From the design for the methanol reactor, the weight of the catalyst could be calculated. The volume of the tubes was found to be 33.608 cubic centimeters, the catalyst density was 0.44 grams per cubic centimeters, and the bed porosity was 0.41.

$$33.608 \text{ m}^3 \left(\frac{1,000,000 \text{ cm}^3}{\text{m}^3} \right) \left(\frac{0.44 \text{ g catalyst}}{\text{cm}^3} \right) (1 - 0.41) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 8724.64 \text{ kg catalyst} \quad (7.3.5)$$

The catalyst volume was constant over time, thus:

$$\frac{8724.64 \text{ kg catalyst}}{56,000,000 \text{ gallons}} = 0.0001559 \text{ kg/gallon} \quad (7.3.6)$$

The two reactors that required cooling fluid, the zinc oxide bed reactor and the methanol reactor, required distinctly different quantities when the design had been completed. The methanol reactor was found to require 1,000,000 kg per hour of coolant, while the zinc oxide bed required only 260 kg per hour. Assuming these values to be accurate, the ratio of kilograms of coolant to gallon of methanol produced would be as follows:

$$\frac{(1,000,000 \text{ kg/hr}) + (260 \text{ kg/hr})}{19178 \text{ gal/hr}} = 52.16 \text{ kg/gallon} \quad (7.3.7)$$

If the price of coolant was set according to Go Glycol Pros, a site selling various Dowtherm coolants in bulk, the price per kilogram would be \$0.9946 per kilogram, for a price of about 52 dollars spent on coolant per gallon produced^[7.1]. That was not economically viable, and the vast discrepancy between the amounts of coolant required for the two reactors suggested the possibility of an error there. For a more reasonable economic approximation, it was assumed that the methanol reactor required nine times as much coolant as the zinc oxide bed reactor— a substantial increase, but one not to the extent currently represented by the reactor designs. With that assumption, the ratio was amended to a far more reasonable one.

$$260 \frac{\text{kg}}{\text{hr}} * (9_{(\text{For MeOH})} + 1_{(\text{For ZnO})}) * (\frac{1}{19178 \text{ gal/hr}}) = 0.1356 \frac{\text{kg}}{\text{gal}} \quad (7.3.8)$$

Utilities

Waste management was needed for both the solid and aqueous streams exiting the reactor system. The organic streams included the wastewater from the spray quench and the purge stream following the flash drum out of the methanol reactor. There were also two waste streams from the distillation column, a vapor release from the storage tank and the bottoms stream from the distillation column. Of those four streams, two were gasses— the purge stream following the flash drum and the vapor release from the storage tank. For the purposes of economic analysis, these were treated as though they were aqueous and sent to wastewater treatment under the assumption that gas capture or some other remediation would be comparable and the gas streams would not just be released into the atmosphere. Two of the streams were also from the downstream plant rather than the upstream plant, which had a different production time that had to be taken into account. Accordingly, this calculation was performed in Table 7.3.1. Fluids treatment cost \$0.31 per kilogram of waste.

Table 7.3.1 Aqueous and Pseudo-Aqueous Waste Disposal

Waste Stream	Spray Quench	Purge	Vapor Release	Bottoms Stream
State	Liquid	Gas	Gas	Liquid
Flow rate	3217.83	25.3	13.61	101.5

(kmol/hr)				
Primary component	Water	CO + H ₂ (equal split)	MeOH	CO
Approximate MW (g/mol)	18.02	15.015	32.04	28.01
Processing Region	Upstream	Upstream	Downstream	Downstream
Gallons MeOH produced per hr	19178	19178	7000	7000
Kg per gallon produced	3.024	0.0198	0.0623	0.406

Thus, a total of 3.512 kg of aqueous waste treatment was required per gallon of methanol produced.

Solid waste was disposed of in a landfill, at a cost of \$0.19 per kilogram. The only stream disposed of this way was the solid zinc chloride stream following the zinc oxide bed.

$$2.3529 \frac{\text{kmol}}{\text{hr}} \left(\frac{136.29 \text{ kg}}{\text{kmol}} \right) \left(\frac{1}{19178 \text{ gal/hr}} \right) = 0.01672 \text{ kg/gal} \quad (7.3.9)$$

Electricity was also supplied for the pumps and compressors. 1000 Hp total were required for the compressors, with an additional 200 Hp for the pumps responsible for the inlet reacting water stream to the solar thermal reactor, 150 Hp for the pumps supplying water to the spray quench, and 7.94 Hp for the pump to the downstream distillation column.

$$\frac{(1000+200+150 \text{ Hp}) \left(\frac{0.7457 \text{ kW}}{\text{Hp}} \right) (2920 \frac{\text{hrs}}{\text{year}}) + (7.94 \text{ Hp}) \left(\frac{0.7457 \text{ kW}}{\text{Hp}} \right) (8000 \frac{\text{hrs}}{\text{year}})}{56,000,000 \text{ gallons/year}} = 0.05334 \text{ kW} - \text{hr} \quad (7.3.10)$$

The cooling and heating fluids involved in the heat exchanger also needed to be supplied as utilities. For the economic analysis, the design of the heat exchangers was used for the amounts and identities of the heat exchanger utility streams, rather than the base-case from Energy Analyzer as outlined in section 6. Combustion gas and cooling water were fed as utilities into the heat exchangers, with steam being produced. It was assumed that the steam was low pressure, and that it could be sold. The steam was therefore taken as a credit, rather than a price. Low pressure steam was given at \$0.00786 per kg, combustion gas was treated as having the same price as natural gas (\$0.005 per cubic foot), and water was supplied for both the process and cooling/heating utilities at \$0.019 per cubic meter.

Combustion gas was supplied at a rate of 88.38 cubic meters per hour.

$$88.38 \frac{m^3}{hr} * (\frac{35.31 ft^3}{m^3}) (\frac{1}{19178 gal/hr}) = 0.1627 ft^3/gal \quad (7.3.11)$$

The process water was taken to refer to the water entering the reactor directly as one of the components to be used in the reaction, as well as the water supplied to the spray quench.

$$(21402.2 \frac{kg}{hr} + 3234 \frac{kmol}{hr} * \frac{18.02 kg}{kmol}) * \frac{1}{19178 gal/hr} = 4.155 kg/gal \quad (7.3.12)$$

The cooling and heating water for the heat exchangers was supplied at the rates explained in section 5.3.1. The heat exchangers upstream and the condenser and reboiler downstream were all fed either cooling or heating water, assumed to be equal in cost for this analysis.

$$Heat\ Exchangers = (38.86 \frac{m^3}{hr} + 61.17 \frac{m^3}{hr} + 107 \frac{m^3}{hr}) (\frac{1}{19178 gal/hr}) = 0.0108 m^3/gal \quad (7.3.13)$$

$$Condenser/Reboiler = (6297 \frac{m^3}{hr} + 1074 \frac{m^3}{hr}) (\frac{1}{7000 gal/hr}) = 1.053 m^3/gal \quad (7.3.14)$$

Steam was generated by the three heat exchangers in the upstream process. Due to conservation of mass, the same weight of water would still be present following the expansion, just over a larger area. Thus, the mass of water in the liquid phase was equal to the mass of water in the vapor phase following the evaporation.

$$Steam = (38.87 \frac{m^3 liq}{hr} + 61.17 \frac{m^3 liq}{hr} + 107 \frac{m^3 liq}{hr}) (\frac{10^3 kg}{m^3 liq}) (\frac{1}{19178 gal/hr}) = 10.796 kg/gal \quad (7.3.15)$$

Carbon Credit

A carbon offset credit was added to the economics model to express the credit that would need to be given in order for this process to maintain the current selling price of \$1.76 per gallon of methanol with a 12.5% IRR. Although this calculation has been provided in the variable cost section, this calculation was performed following all the rest of the economics calculations in an iterative manner. The problem statement stated that a standard industrial process produced approximately 2.2 kg of carbon dioxide per kg of methanol.

$$2.2 \frac{kg CO_2}{kg MeOH} (\frac{792 kg MeOH}{m^3}) (\frac{1 m^3}{264.172 gal}) = 6.5957 kg CO_2/gal \quad (7.3.16)$$

The net amount of carbon dioxide produced by the process detailed in this report could be described as the sum of the amounts of carbon dioxide produced by the water gas shift reaction and the carbon dioxide consumed in the production of raw methanol. Using the mole fractions and the molar flow rates of the streams into and out of these reactors, the amount of carbon dioxide produced and then consumed was calculated. 0.1023 kmol/hr of CO₂ were produced in the water gas shift reaction, while 0.0979 kmol/hr were consumed by the methanol reactor for a net carbon dioxide production rate of 0.0044 kmol/hr.

$$0.044 \frac{\text{kmol}}{\text{hr}} \left(\frac{44.01 \text{ kg}}{\text{kmol}} \right) \left(\frac{1}{19178 \text{ gal/hr}} \right) = 0.00001 \text{ kg CO}_2/\text{gal} \quad (7.3.17)$$

This value was deemed negligible compared to the amount of carbon dioxide produced in a standard process, such that the carbon dioxide production that was avoided was equal to that of a standard process, 6.5957 kg/gallon, or 0.006596 metric tons per gallon. Using an iterative, guess-and-check method, the offset credit per metric ton was varied and the simulation run (with the base case of 12.5% IRR) to establish the necessary credit for the price of methanol to equal \$1.76 per gallon. Using this method, it was found that a credit of \$510 per metric ton of carbon dioxide resulted in the desired methanol price.

7.4 Fixed Cost

Insurance and local taxes were assumed to be 2.0% of the capital investment. Royalties were assumed to be \$0.0265 per gallon, as defined in the problem statement. The rest of the overhead and operating expenses were taken into account on a per operator basis, where all wages, benefits, maintenance and overhead were included in a fixed sum of \$150k per operator.

For a fluid-solid processing plant producing 500 tons a day, two operators per process section per shift should be employed. A shift was regarded to be eight hours. In the upstream processing plant, the sections were divided up into the two heliostat towers and fields, the solar thermal reactor, the spray quench, the zinc oxide bed reactor, and the methanol reactor. Since the upstream process operated for eight hours a day, one shift was needed for weekdays, one for weekends, and one additional shift in case of illness was required. Thus, for the upstream processing plant, 36 operators were needed.

$$6 \text{ sections} * 2 \text{ operators/shift} - \text{section} * 3 \text{ shifts} = 36 \text{ operators} \quad (7.4.1)$$

The methanol purification section had only one section, the distillation column, but it operated throughout the day. Thus, three shifts were needed for weekdays in addition to the shift for weekends and the additional shift. Thus, 10 operators were required.

$$1 \text{ section} * 2 \text{ operators/shift} - \text{section} * 5 \text{ shifts} = 10 \text{ operators} \quad (7.4.2)$$

Overall, 46 operators were therefore required.

7.5 Cash Flow

The full cash flow analysis utilized the cost approximations for capital cost, variable cost, and fixed cost. A few additional economic elements were also taken into account at this final step. The cost of capital, expressing the interest on any loans required, was assumed to be 8.5%. Inflation for both costs and product price was assumed to be 4.0% as established earlier. The Weimer Project Economics Excel file was initially designed for a plant lifetime of 15 years. As the process discussed in this report was intended for a 25 year lifetime, the calculation file was expanded. It was assumed that the plant was operated at 50% capacity upon startup, 75% the following year, and 100% all subsequent years. The salvage percentage was 10%. Accounts receivable were given as 30 days. Construction was allotted to a period of two years prior to startup. From the problem statement, 24% income tax was utilized, and as discussed earlier a 12.5% IRR was utilized as the base case. Finally, land use was calculated as being three times the area of all the heliostat fields and priced at \$1000 per acre. The full Excel file has been provided in Appendix N for reference in more detail. Figure 7.5.1 expressed the base-case cash flow for every year of process operation. Figure 7.5.2 expressed a cumulative cash flow, again using the base case IRR.

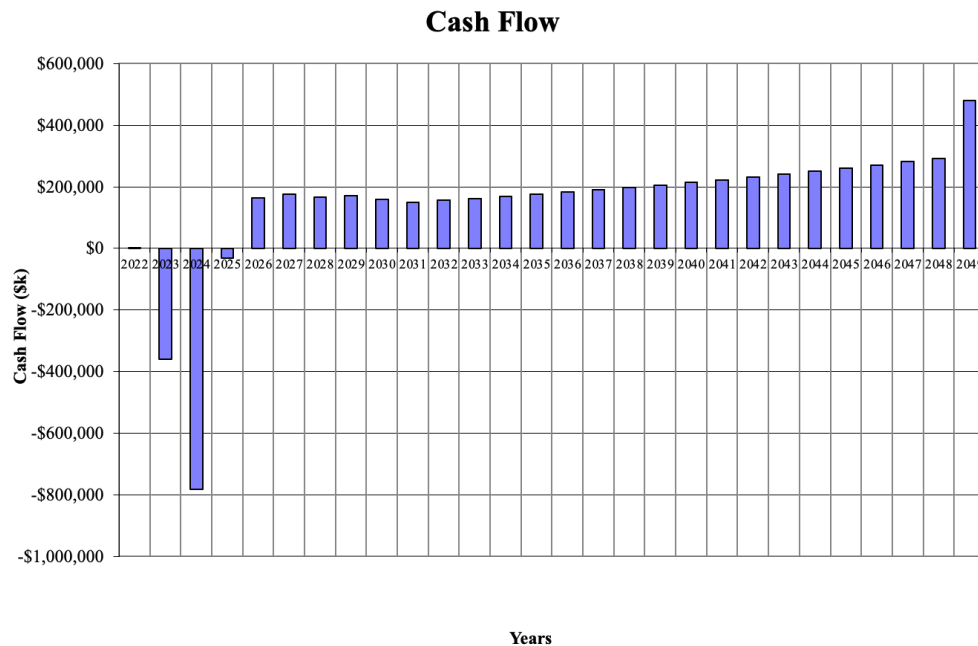


Figure 7.5.1 Base Case (12.5% IRR) Cash Flow Per Year over the Lifetime of the Plant.

Even with the high carbon dioxide reduction credit, the base-case cumulative cash flow chart demonstrated that the process would not experience a net positive cash flow until 2033, the ninth

year of plant operation. While a net positive was observed after that, the probability of a process with a substantial net-negative cash flow for so much of its operational period might be considered unlikely to succeed if actually built.

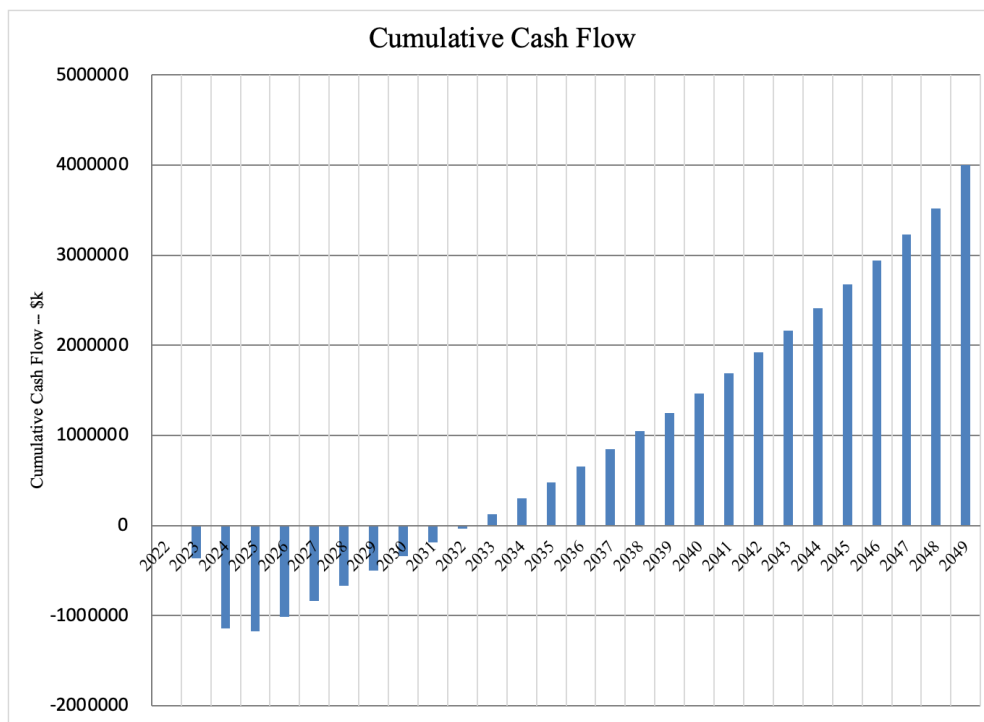


Figure 7.5.2 Base Case (12.5%) IRR Cumulative Cash Flow

7.6 Sensitivity Analysis

Following the calculation of the carbon credit as discussed in section 7.3, sensitivity analysis was performed and data was collected regarding the various economic factors. ROI (return on investment), PBP (pay-back period), and end-of-period NPV (cash flow at the end of each period) was determined for a variety of different IRR (investor's rate of return) values other than the base case of 12.5%. These values were summarized in Table 7.6.1. This table demonstrated that the price per gallon would need to significantly increase in order to increase the IRR value. With increasing methanol price, IRR, ROI, and NPV were all shown to increase, and PBP was shown to decrease. Economically, those changes were all considered preferable; however, market standard prices and the willingness to purchase more expensive products when less expensive might be available from other sources suggests that an optimization should be performed.

Table 7.6.1 Economic Factors Associated with IRR Values

IRR	12.5%	15%	20%	25%
ROI	11.8%	14.5%	20.5%	27.3%
PBP (years)	8.5	6.9	4.9	3.7
NPV (at end of each period)	\$439,208 k	\$759,173 k	\$1,618,085 k	\$2,328,673 k
Price of MeOH per gallon	\$1.76	\$2.46	\$4.07	\$5.91

Sensitivity analyses for the price of methanol were performed from the base case with a 50% variability for the following economic variables: overall cost of capital, cost of biomass feed, cost of methane feed, number of operators, carbon credit, and IRR. The results of these studies were plotted in Appendix N to be viewed in full. It was observed that a 50% variability in methane price resulted in a methanol range from \$1.67 to \$1.86, while variability of biomass price resulted in a methanol price range between \$1.71 and \$1.82. The number of operators had a similarly low impact on the price of methanol, with a range between \$1.69 and \$1.83. Of the studies performed, carbon credit (Figure 7.6.1) was found to have the most significant impact on methanol price, with 50% variability resulting in a range of methanol price between \$0.05 and \$3.47. The IRR study (Figure 7.6.2) was also comparable in its influence on the price of methanol, ranging between approximately \$0.35 and \$3.65. The TDC study (Figure 7.6.3) showed similar results, with a price range between \$0.28 and \$3.25. This suggested the probability of these factors significantly impacting the price of methanol required for an IRR of 12.5%, but as mentioned in section 7.5 that still does not necessarily result in a profitable process design.

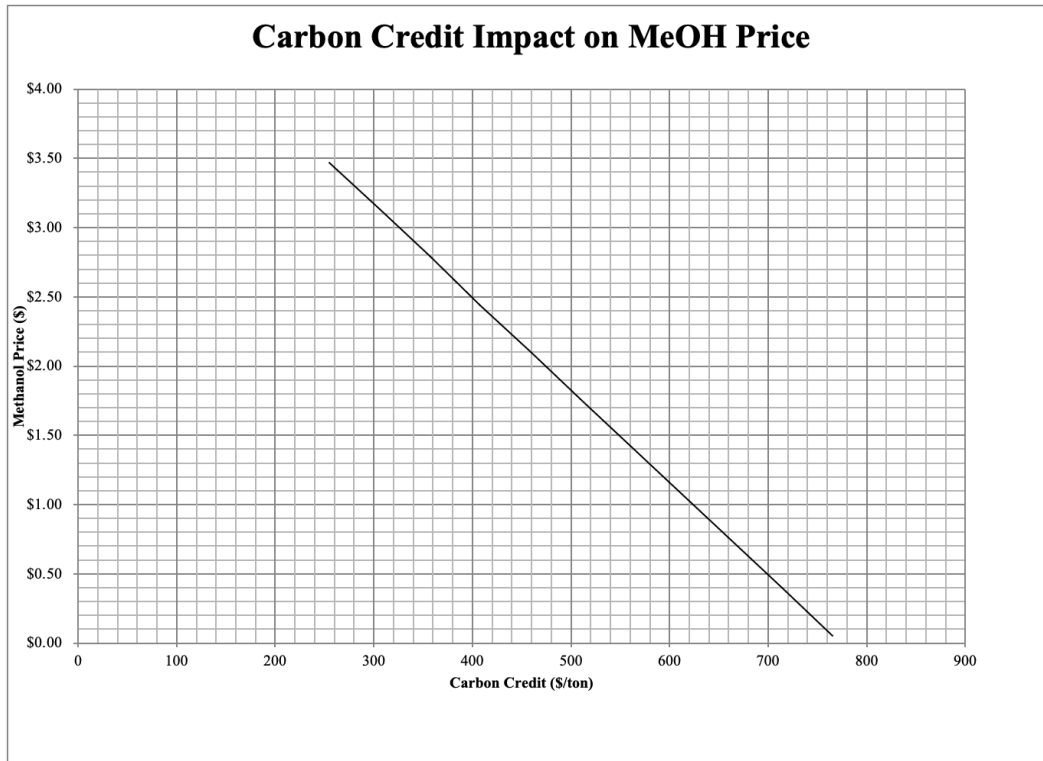


Figure 7.6.1 Visual Representation of a 50% Variability of Carbon Credit on Methanol Price

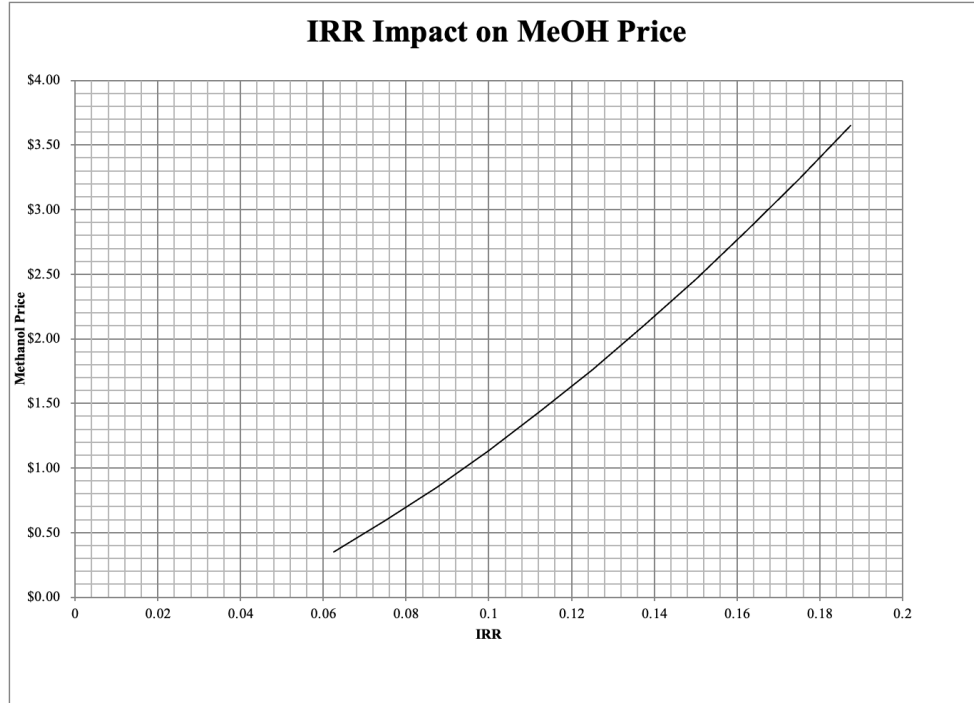


Figure 7.6.2 Visual Representation of a 50% Variability of IRR on Methanol Price

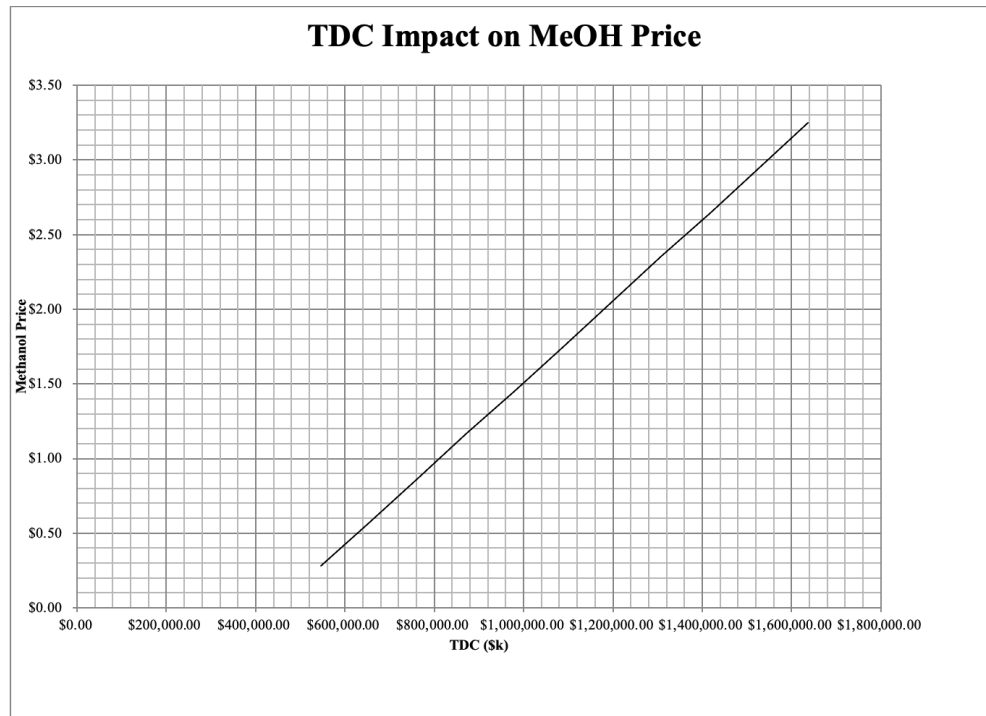


Figure 7.6.3 Visual Representation of a 50% Variability of TDC on Methanol Price

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Table of Nomenclature

Symbol	Definition	Units
a_A	Stoichiometric coefficient of gaseous reactant	N/A
a_c	Surface area of carbon particles	m^2
a_S	Stoichiometric coefficient of solid reactant	N/A
A	Surface area of heat transfer	m^2
A_c	Cross sectional area of tube	m^2
$A_{c, total}$	Cross sectional area of all tubes	m^2
A_i	Cross sectional area of reactor	m^2
b_i	Adsorption constant of species i	Variable
C_A	Concentration of gaseous reactant in porous pellet	$\frac{mol}{l^3}$
C_{S0}	Initial concentration of solid reactant in pellet	$\frac{mol}{l^3}$
C_{S0}'	Initial concentration of solid reactant in grain	$\frac{mol}{l^3}$
C_p	Heat capacity	$\frac{J}{gK}$
C_{pc}	Heat capacity of coolant	$\frac{J}{gK}$
d_c	Cutoff diameter	m
D	Inner tube diameter	m
D_A'	Diffusion coefficient of gaseous reactant in grain pellet	$\frac{l^2}{t}$
D_p	Catalyst particle diameter	m
D_o	Outer tube diameter	m
D_R	Diameter of reactor	m

D_T	Diameter of tower	m
E_i	Activation energy of reaction i	$\frac{kJ}{mol}$
F_i	Molar flow rate of species i	$\frac{kmol}{hr}$
h_i	Convective heat transfer coefficient	$\frac{W}{m^2K}$
k_i	Kinetic constant of reaction i	Variable
k_g	Conductivity of gas phase	$\frac{W}{mK}$
K_i	Equilibrium constant of reaction i	Variable
L	Length	m
m_c	Mass flowrate of coolant	$\frac{kg}{hr}$
MW_i	Molecular weight of species i	$\frac{g}{mol}$
n	Number of tubes	N/A
n	Stoichiometric coefficient	N/A
n_c	Number of particles per cubic meter	m^{-2}
N	Number of trays	N/A
N_e	Number of effective turns within the cyclone	N/A
N_{min}	Minimum number of stages	N/A
P	Pressure	bar or kPa
Q	Molar flow rate	$\frac{kmol}{hr}$
r_c'	Unreacted core radius	m
r_s'	Grain radius	m
R	Gas constant	$\frac{J}{molK}$

R_{min}	Minimum reflux ratio	N/A
R_0	Carbon particle radius	m
t	Time	Variable
T_i	Temperature of unit i	K
U	Coolant overall heat transfer coefficient	$\frac{W}{m^2 K}$
V	Volume	m^3 or L
V_c	Volume of carbon particle	m^3
v	Velocity of gas	$\frac{m}{s}$
X	Conversion	N/A
v_i	Molar flow rate of species i	$\frac{kmol}{hr}$
ΔH	Change of enthalpy	$\frac{kJ}{mol}$
ΔH_f^o	Heat of formation @ T = 298K	$\frac{kJ}{mol}$
Δr	Thickness of reactor wall	m
ε_c	Emissivity of carbon particles	N/A
μ	Gas viscosity	$kPa \cdot s$
v_g	Velocity of gas	$\frac{m}{s}$
ρ	Gas density	$\frac{kg}{m^3}$
ρ_c	Catalyst density	$\frac{g}{cm^3}$
σ	Boltzmann constant	$\frac{W}{m^2 K^4}$
ϕ	Catalyst porosity	N/A

ϕ_b	Bed porosity	N/A
φ	Geometric factor	N/A

Appendices

Appendix A: Initial Material Balance Excel Sheet

Link to Appendix A:

https://docs.google.com/spreadsheets/d/1R2deeaEyIYpZYIZDmo58qZth2ruirxXd/edit?usp=share_link&ouid=107788896093621351211&rtpof=true&sd=true

Appendix B: Initial Energy Balance Excel Sheet

Link to Appendix B:

https://docs.google.com/spreadsheets/d/1sp9dk5DqOgaVHYLZ0hZnVRRk-5LhY6aMKnJ1rTJywRM/edit?usp=share_link

Appendix C: Finalized Aspen Plus File

Link to Appendix C:

https://drive.google.com/file/d/13DsddnMb2RfYPdCq8rZErBh4u3w7kShX/view?usp=share_link

Appendix D: Finalized Aspen HYSYS File

Link to Appendix D:

https://drive.google.com/file/d/1lKK_pw8ynoGH1QeuQAItB_dA0pciNXIX/view?usp=share_link

Appendix E: Solar Thermal Reactor Heat of Reaction Excel File

Link to Appendix E:

https://docs.google.com/spreadsheets/d/18A6vBxv4ReOKMfFwxC55N4YLoTN2UK0v/edit?usp=share_link&ouid=107788896093621351211&rtpof=true&sd=true

Appendix F: Solar Thermal Reactor Matlab Code

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```
%Methanol Solar Thermal Reactor Design
%Katie Crocker
clear figure
clear
clc
```

Length Domain

```
L_tot = 25; %m
Z_domain = [0 : 0.1 : L_tot];
```

Initial Conditions

```
%Constants
P=35; %bar
Tw=1450; %C
%Stream 2: Mixed recycle and feed streams for CH4, Biomass
%Stream 1: Entering water stream

%Neutral Species
F_Ash= 39.2073*1000;           %mol/hr, stream 2
F_N2=40.2834*1000;           %mol/hr, stream 2
F_MeOH=7.42072*1000;         %mol/hr, stream 2
F_CO2=0.00361055*1000;       %mol/hr, stream 2
%Neglect reactions of S and Cl2
F_S_in=0.0825*1000;          %mol/hr, stream 2
F_H2S_in=0;                  %mol/hr, stream 2
F_Cl2_in=2.2704*1000;        %mol/hr, stream 2
F_HCl_in=0;                  %mol/hr, stream 2

%Reacting Species
F_Cellulose_in= 112.939*1000; %mol/hr, stream 2
F_Lignin_in= 32.3862*1000;    %mol/hr, stream 2
F_CH4_in=848.1*1000;         %mol/hr, stream 2
F_C_in=6*F_Cellulose_in+10*F_Lignin_in+F_CH4_in; %mol/hr, formed by
decomposition

F_H2O_in=(0.0275975+1188)*1000+5*F_Cellulose_in+3*F_Lignin_in; %mol/
hr, stream 2 + 1 + decomposition
```

```

F_CO_in=207.99*1000; %mol/hr, stream 2
F_H2_in=(231.294*1000)+2*F_CH4_in+3*F_Lignin_in; %mol/hr, stream 2 +
    decomposition

%Temperatures
Tg_in=25+273; %K, room temperature
Tc_in=25+273; %K, room temperature

IC = [F_C_in F_H2O_in F_CO_in F_H2_in Tg_in Tc_in];

```

Solve ODE

```
[Xsol, Ysol] = ode45('STRD_ODE_KC_Simplified', Z_domain, IC);
```

Data Handling

Extracting solutions for each variable

```

F_C_sol=Ysol(:,1);
F_H2O_sol=Ysol(:,2);
F_CO_sol=Ysol(:,3);
F_H2_sol=Ysol(:,4);
Tg_sol=Ysol(:,5);
Tc_sol=Ysol(:,6);

%Uncomment to give as an output when code is run
%"Finished"

```

Plotting

```

fig1 = figure(1);
set(fig1, 'Name', 'Gas Temperature');
area(Xsol, (Tg_sol));
xlabel('Distance Z (m)');
ylabel('Temperature (K)');
title('Gas Temperature');

fig2= figure(2);
set(fig2, 'Name', 'Carbon Flowrate');
area(Xsol, F_C_sol/1000);
xlabel('Distance z (m)');
ylabel('kmol/hr');
title('Carbon Flowrate');

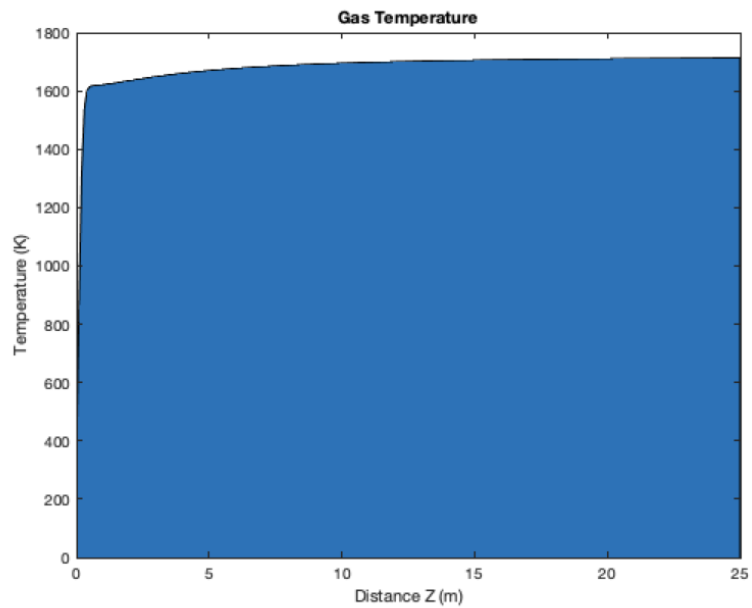
fig3= figure(3);
set(fig3, 'Name', 'Carbon Temperature');
area(Xsol, Tc_sol);
xlabel('Distance z (m)');
ylabel('Temperature (K)');
title('Particle Temperature');

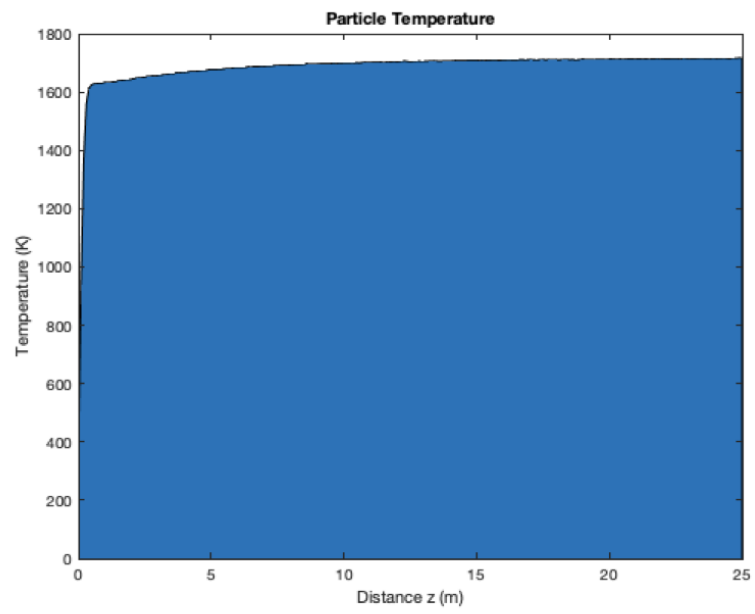
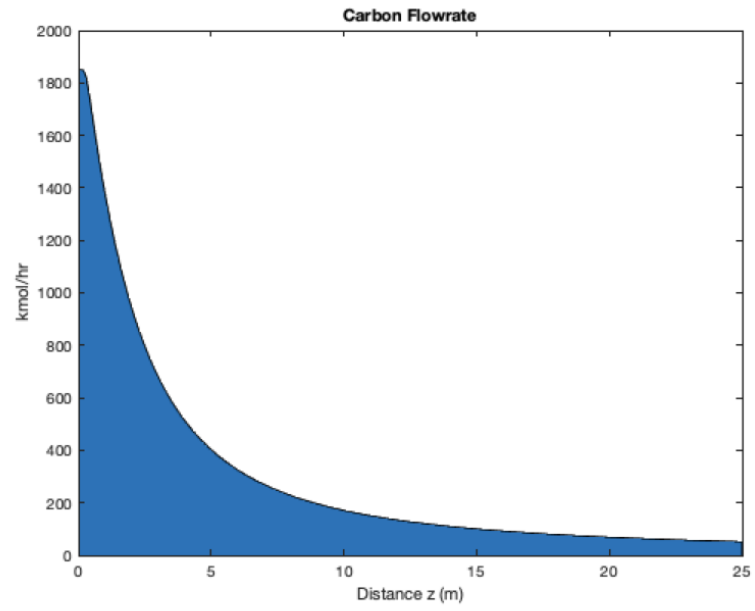
```

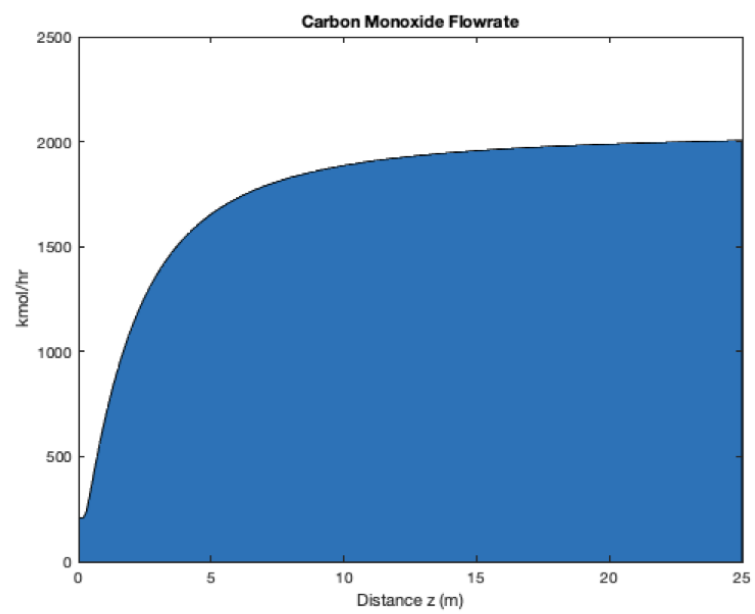
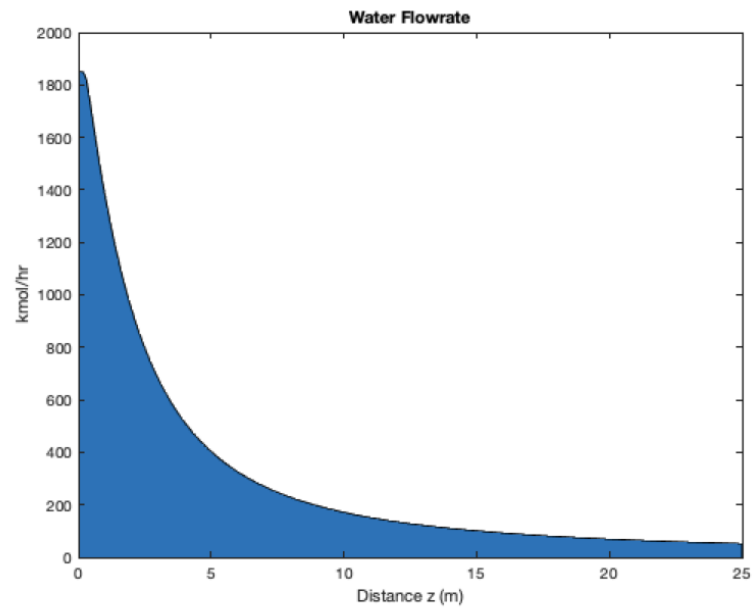
```
fig4= figure(4);
set(fig4, 'Name', 'Water Flowrate');
area(Xsol, F_H2O_sol/1000);
xlabel('Distance z (m)');
ylabel('kmol/hr');
title('Water Flowrate');

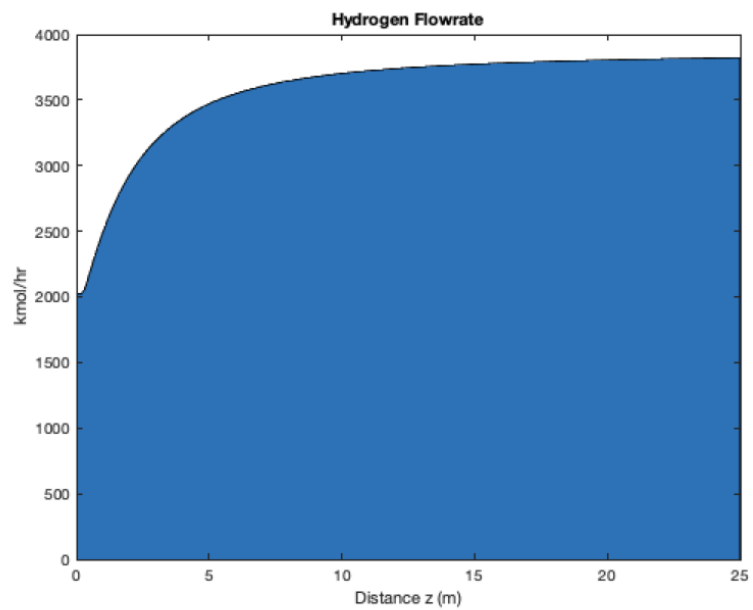
fig5= figure(5);
set(fig5, 'Name', 'Carbon Monoxide Flowrate');
area(Xsol, F_CO_sol/1000);
xlabel('Distance z (m)');
ylabel('kmol/hr');
title('Carbon Monoxide Flowrate');

fig6= figure(6);
set(fig6, 'Name', 'Hydrogen Flowrate');
area(Xsol, F_H2_sol/1000);
xlabel('Distance z (m)');
ylabel('kmol/hr');
title('Hydrogen Flowrate');
```









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```
function [per_ode] = STRD_ODE_KC_Simplified(X,Y)
```

Output Variables

```
F_C=Y(1);  
F_H2O=Y(2);  
F_CO=Y(3);  
F_H2=Y(4);  
Tg=Y(5);  
Tc=Y(6);
```

Inlet Flow Rates

```
%Neutral Species  
F_Ash= 39.2073*1000;           %mol/hr, stream 2  
F_N2=40.2834*1000;            %mol/hr, stream 2  
F_MeOH=7.42072*1000;          %mol/hr, stream 2  
F_CO2=0.00361055*1000;        %mol/hr, stream 2  
%Neglect reactions of S and Cl2, so assume constant  
F_S=0.0825*1000;              %mol/hr, stream 2  
F_H2S=0;                      %mol/hr, stream 2  
F_Cl2=2.2704*1000;            %mol/hr, stream 2  
F_HCl=0;                      %mol/hr, stream 2  
  
%Decomposing Species-- assume instantaneous decomposition into carbon  
upon  
%entering the reactor  
F_Cellulose_in= 112.939*1000;  %mol/hr, stream 2  
F_Lignin_in= 32.3862*1000;     %mol/hr, stream 2  
F_CH4_in=848.1*1000;           %mol/hr, stream 2  
%Reacting Species  
F_C_in=6*F_Cellulose_in+10*F_Lignin_in+F_CH4_in; %mol/hr, formed by  
decomposition  
F_H2O_in=((0.0275975+1188)*1000)+5*F_Cellulose_in+3*F_Lignin_in; %mol/  
hr, stream 2 + 1 + decomposition  
F_CO_in=207.99*1000; %mol/hr, stream 2  
F_H2_in=(231.294*1000)+2*F_CH4_in+3*F_Lignin_in; %mol/hr, stream 2 +  
decomposition  
  
FgTot=(F_S+F_H2S+F_Cl2+F_HCl+F_H2O+F_CO+F_H2+F_N2+F_MeOH+F_CO2); %mol/  
hr, Gas phase species only (no ash or C)
```

```

%Arbitrary Constants
%Is there a way to solve for the velocity?
vg=0.25; %m/s, velocity of gas, arbitrary (!) (dt/dz=1/vg)
Area=0.25; %m^2, cross-sectional area, arbitrary (!)
L_Tot=25; %m, copy over from ODE solver, arbitrary (!)

```

Reaction Rates

```

P=35; %bar
R=8.314; %J/mol-K

%Neglect rates of decomposition by assuming that only carbon enters
the
%reactor
%Neglect reaction rates of S, Cl2

%Reaction of C and H2O to CO and H2
%C
%Reaction k constants
ka=2.51*10^3; %1/bar-s
kb=6.74*10^(-2); %1/bar
kc=3.04*10^(-1); %1/bar
Ea=112.6*1000; %J/mol
Eb=-37.3*1000; %J/mol
Ec=-36.6*1000; %J/mol
Ka=ka*exp(-Ea/(R*Tc)); %1/bar-s
Kb=kb*exp(-Eb/(R*Tc)); %1/bar
Kc=kc*exp(-Ec/(R*Tc)); %1/bar
phi=4.3;
%Partial Pressures
P_H2O=P*(F_H2O/FgTot); %bar
P_H2=P*(F_H2/FgTot); %bar
%Rate of reaction
KO=(Ka*P_H2O)/(1+(Kb*P_H2O)+(Kc*P_H2)); %1/sec
r=-KO/vg*(F_C)*sqrt(1-(phi*log(F_C/F_C_in))); %mol/m-hr
rC=r; %mol/m-hr

%H2O
rH2O=r; %mol/m-hr
%CO
rCO=-r; %mol/m-hr
%H2
rH2=-r; %mol/m-hr

```

Energy Balances

```

Tw=1450+273; %K
%Heat of Reaction (Calculations in Excel File)
HC=161.857190*1000; %J/mol

%Particle Energy Balance
%Species: C, Ash

```

```

MWC=12.01; %g/mol
MWAsh=60.086; %g/mol
CpC=21.1751-0.812428*(Tc/1000)+0.448537*((Tc/1000)^2)-0.043256*((Tc/1000)^3)-0.013
((Tc/1000)^4); %J/mol-K
CpAsh=0.04236063; %J/mol-K, constant
FcCpc=(F_C*CpC)+(F_Ash*CpAsh); %J/hr-K

%Constants from Dahl paper
theta=5.67*10^(-8); %W/m2-K4
epsilon=1;
ac=3.1*10^(-8); %m2
Vc=5.2*10^(-13); %m3
rhoc=2270*1000; %g/m^3
Ro=5*10^(-5); %m
nc=(F_C*MWC+F_Ash*MWAsh)/(vg*3600*Area*Vc*rhoc); %1/m3, particles per
m3

%Heat transfer coefficient
kg=261.19/1000; %W/m-K thermal conductivity, approximate as CH4 at
T=1450 C
hp=kg/Ro; %W/m2-K

Ap=(HC*rC)/FcCpc; %K/hr
Bp=(epsilon*theta*3600*ac*Area*nc)/(FcCpc)*(Tw^4-Tc^4); %K/m,
radiative heat transfer to particles from wall
Cp=-hp*3600*ac*Area*nc/(FcCpc)*(Tc-Tg); %K/m, convective heat transfer
to gas from particles
dTcdz=Ap+Bp+Cp; %K/m

%Gas Energy Balance
%Species:
%Constant Species: S, H2S, Cl2, HCl, N2, MeOH, CO2
%Reacting Species: H2O, CO, H2

%Molecular Weights
MWS=32.07; %g/mol
MWH2S=34.09; %g/mol
MWCl2=70.90; %g/mol
MWHCl=36.46; %g/mol
MWN2=28.02; %g/mol
MWMeOH=32.05; %g/mol
MWCO2=44.01; %g/mol
MWH2O=18.02; %g/mol
MWCO=28.01; %g/mol
MWH2=2.02; %g/mol
%Heat Capacities (See Excel)
CpS=-37.9335+133.242*(Tg/1000)-95.3245*((Tg/1000)^2)+24.0094*((Tg/1000)^3)+7.65453
((Tg/1000)^4); %J/mol-K
CpH2S=51.22136+4.147486*(Tg/1000)-0.643566*((Tg/1000)^2)+0.041621*((Tg/1000)^3)-10
((Tg/1000)^4); %J/mol-K
CpCl2=((33.6*10^-3)+(1.367*10^-5)*Tg-
(1.607*10^-8)*Tg^2+(6.743*10^-12)*Tg^3)*1000; %J/mol-K
CpHCl=((29.13*10^-3)-(0.1341*10^-5)*Tg+(0.9715*10^-8)*Tg^2-
(4.335*10^-12)*Tg^3)*1000; %J/mol-K

```

```

CpN2=19.50583+19.88705*(Tg/1000)-8.598535*((Tg/1000)^2)+1.369784*((Tg/1000)^3)+0.5
((Tg/1000)^4); %J/mol-K
CpMeOH=0.10968*1000; %J/mol-K-- not a function of T
CpCO2=58.16639+2.720074*(Tg/1000)-0.492289*((Tg/1000)^2)+0.038844*((Tg/1000)^3)-6.
((Tg/1000)^4); %J/mol-K
CpH2O=0.049509829*1000; %J/mol-K-- not a function of T
CpCO=((28.95*10^-3)+(0.411*10^-5)*Tg+(0.3548*10^-8)*Tg^2-
(2.22*10^-12)*Tg^3)*1000; %J/mol-K
CpH2=((28.84*10^-3)+(0.00765*10^-5)*Tg+(0.3288*10^-8)*Tg^2-
(0.8698*10^-12)*Tg^3)*1000; %J/mol-K

%Weighted MW of the gas
MWg=((F_S*MWS)+(F_H2S*MWH2S)+(F_C12*MWC12)+(F_HCl*MWHCl)+(F_CO*MWCO)+(F_H2*MWH2)+(
FgTot; %g/mol
FCp=(F_S*CpS)+(F_H2S*CpH2S)+(F_C12*CpC12)+(F_HCl*CpHCl)+(F_CO*CpCO)+(F_H2*CpH2)+(F
hr-K
Cpg=FCp/FgTot; %J/mol-K

%Constants
Tf=Tw; %K
di=0.076; %m
mu=0.04650; %cP, viscosity, approximate as CH4 at T=1450 C
mu_g=mu*3600; %g/m-hr
hw=0.034*(kg/di)*(FgTot*MWg*di/Area/mu_g)^(0.8)*(Tg/
Tf)^(0.8)*(Cpg*mu_g/(kg*3600)/MWg)^(0.4)*(L_Tot/di)^(0.1); %W/m2-K

Ag=(HC*rC); %J/m-hr
Bg=hw*3600*pi*di*(Tw-Tg); %J/m-hr, convective heat transfer from the
walls
Cg=hp*ac*F_C*MWC*(Tc-Tg)/(vg*Vc*rhoc); %J/m-hr, convective heat
transfer from the particles
dTgdz=(Ag+Bg+Cg)/FCp; %K/m

```

Sending ODE solutions back to array for further iteration

```

dF_C=rC;
dF_H2O=rH2O;
dF_CO=rCO;
dF_H2=rH2;
dTg=dTgdz;
dTc=dTcdz;
per_ode = [dF_C;dF_H2O;dF_CO;dF_H2;dTg;dTc];

```

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Appendix G: Catalytic Gas Cleaning Bed Matlab Code

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`% HW 8 Reactor Kinetics`

Volume Domain

```
V_tot = 4.2*1000; %L
V_domain = [0 : 1 : V_tot];
```

Initial Conditions

```
%Pi = 3500; % Initial pressure kPa
FZnO_in = 2.35 * 1000; % mol/hr
FHCl_in = 4.54 * 1000; % mol/hr
FH2S_in = 0.0825 * 1000; % mol/hr
FZnS_in = 0; % mol/hr
FH2O_in = 0; % mol/hr
FZnCl2_in = 0; % mol/hr
T_coolant_in = 550; % Kelvin. Found this from a
    Heuristic temp range
T_coolant_in = 635; %Celsius
T_reactor_in = 650; %Celsius
IC = [FZnO_in FHCl_in FH2S_in FZnS_in FH2O_in FZnCl2_in T_coolant_in
    T_reactor_in]; % Array all inlet conditions
```

Solve ODE

```
[Xsol, Ysol] = ode45('ZnOBed', V_domain, IC);
```

Data Handling

Extracting solutions for each variable

```
FZnO_sol = Ysol(:,1);
FHCl_sol = Ysol(:,2);
FH2S_sol = Ysol(:,3);
FZnS_sol = Ysol(:,4);
FH2O_sol = Ysol(:,5);
FZnCl2_sol = Ysol(:,6);
T_coolant_sol = Ysol(:,7);
T_reactor_sol = Ysol(:,8);
%P_sol = Ysol(:,9);
```

Plotting

```
%fig1= figure(1);
%set(fig1, 'Name', 'Pressure');
%area(Xsol, P_sol);
xlabel('Volume (L)');
ylabel('Pressure kPa');
%title('Pressure');

fig2 = figure(2);
set(fig2, 'Name', 'ZnO Flowrate');
area(Xsol, (FZnO_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('ZnO Flowrate');

fig3= figure(3);
set(fig3, 'Name', 'HCl Flowrate');
area(Xsol, (FHC1_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('HCl Flowrate');

fig4= figure(4);
set(fig4, 'Name', 'H2S Flowrate');
area(Xsol, (FH2S_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('H2S Flowrate');

fig5= figure(5);
set(fig5, 'Name', 'ZnS Flowrate');
area(Xsol, (FZnS_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('ZnS Flowrate');

fig6= figure(6);
set(fig6, 'Name', 'H2O Flowrate');
area(Xsol, (FH2O_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('H2O Flowrate');

fig7= figure(7);
set(fig7, 'Name', 'ZnCl2 Flowrate');
area(Xsol, (FZnCl2_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('ZnCl2 Flowrate');

fig8= figure(8);
set(fig8, 'Name', 'Coolant Temperature');
```

```
area(Xsol, T_coolant_sol);
xlabel('Volume (L)');
ylabel('Temperature (C)');
title('Coolant Temperature');

fig9= figure(9);
set(fig9, 'Name', 'Reactor Temperature');
area(Xsol, T_reactor_sol);
xlabel('Volume (L)');
ylabel('Temperature (C)');
title('Reactor Temperature');
```

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```

function [per_ode] = ZnOBed(X,Y)

% Output Variables
FZnO = Y(1);
FHCl = Y(2);
FH2S = Y(3);
FZnS = Y(4);
FH2O = Y(5);
FZnCl2 = Y(6);
T_coolant = Y(7);
T_Reactor = Y(8);
%P = Y(9);

%Volume and Flow Rate of Coolant
Volume_Reactor = 4.2*1000; %L
m_c = 260000; % g/hr Flowrate of coolant
dr = 955; %Pellet to Reactor Diameter Ratio

%Heat Capacities
cp_ZnO = 494/1000; %J/kmol-C, solid - no equation
cp_HCl = 29.13*10^-3*T_Reactor + (-0.1341*10^-5)/2*T_Reactor^2 +
(0.9715*10^-8)/3*T_Reactor^3 + (-4.335*10^-12)/4*T_Reactor^4; %J/
kmol-C
cp_H2S = 33.51*10^-3*T_Reactor + (1.547*10^-5)/2*T_Reactor^2 +
(0.3012*10^-8)/3*T_Reactor^3 + (-3.292*10^-12)/4*T_Reactor^4; %J/
kmol-C
cp_ZnS = 469/1000; %J/kmol-C
cp_H2O = 33.46*10^-3*T_Reactor + (0.668*10^-5)/2*T_Reactor^2 +
(0.7604*10^-8)/3*T_Reactor^3 + (-3.5393*10^-12)/4*T_Reactor^4; %J/
kmol-C
cp_ZnCl2 = 739.54/1000; %J/kmol-C

%Heat of Reaction %C = Cold and T = Hot
Tc = 25; %Celsius
Th = 650; %Celsius
Ccp_H2S = 33.51*10^-3*Tc + (1.547*10^-5)/2*Tc^2 +
(0.3012*10^-8)/3*Tc^3 + (-3.292*10^-12)/4*Tc^4; %J/kmol-C, Heat
capacity formula of cold temperature
Hcp_H2S = 33.51*10^-3*Th + (1.547*10^-5)/2*Th^2 +
(0.3012*10^-8)/3*Th^3 + (-3.292*10^-12)/4*Th^4; %J/kmol-C, Heat
capacity formula of hot temperature
Ccp_H2O = 33.46*10^-3*Tc + (0.668*10^-5)/2*Tc^2 +
(0.7604*10^-8)/3*Tc^3 + (-3.5393*10^-12)/4*Tc^4; %J/kmol-C, Heat
capacity formula of cold temperature
Hcp_H2O = 33.46*10^-3*Th + (0.668*10^-5)/2*Th^2 +
(0.7604*10^-8)/3*Th^3 + (-3.5393*10^-12)/4*Th^4; %J/kmol-C, Heat
capacity formula of cold temperature
CpZnO = cp_ZnO * (Tc - Th); %J/mol, I used Mcat since these are solids
CpZnS = cp_ZnS * (Th - Tc); %J/mol
dH1 = Ccp_H2S - Hcp_H2S + CpZnO; %J/mol
dH3 = Hcp_H2O - Ccp_H2O + CpZnS; %J/mol
HfZnO = -350.46 * 1000; %J/mol

```

```

HfZnS = -49.2 * 1000; %J/mol
HfH2S = -19.96 * 1000; %J/mol
HfH2O = -285.84 * 1000; %J/mol
dH2 = (HfH2O + HfZnS) - (HfZnO + HfH2S); %J/mol
H_rO1 = dH1 + dH2 + dH3; %J/mol, Heat of Reaction

%Reactor Specs
%P = 3500; %kPa
Dp = 0.0036; % m, Pellet Diameter
D = Dp * dr; %m, tube diameter
Do = D + 0.02; %m, . Outside diameter of Reactor (considers wall
thickness)
A_c = pi()*(D/4)^2; % m^2, Tube cross sectional area
L = ((Volume_Reactor)/1000)/(A_c); %m, Tube Length
R = 8.314; % J/mol-K

```

ODE Definitions

```

%Stoicheometric Coeffecients
aa = 1; %Stoicheometric coeffecient of gas reagent
as = 1; %Stoicheometric coeffecient of solid reagent

%Miscellaneous
Dal = ((1.67 * 10^-6)*(100)^2)/60 ; %Diffusivity of H2S gas, cm^2/min
V_Reactor = Volume_Reactor * 1000; %cm^3

%Reactant Concentration
Ci = (0.0825 * 1000)/V_Reactor; %Initial concentration of H2S gas in
pellet, mol/cm^3
CH2S = FH2S/V_Reactor; %Variant concentration of H2S gas in pellet,
mol/cm^3
Csol = (6.89 * 10^-2)/100; %ZnO concentration in grain (inital) mol/
cm^3

%Grain Radius
rs1 = 2.99*10^-6; %Initial Grain Radius, cm
rc1 = (CH2S/Ci) * rs1; %Variant grain radius, cm

% Rate Constants
k1 = 9.46*10^-2 * exp( -7236/(R * T_Reactor)) * 1000; %cm^4/mole-min

% Reaction Rates
drcdt = as * k1* CH2S/(1 - ((aa* k1 * Csol * rc1)/Dal)*(1 - (rc1/
rs1))); %cm/min
rO2 = drcdt * Ci/rs1; %mol/min-cm^3Reaction Rate, using relationship
of rc1 and taking derivative
rO1 = ((rO2/1000)*60)/(10^-3); %kmol/hr-L

% Species Material Balances
rZnO = -rO1; %Reactant
rHCl = -2*rO1; %Reactant
rH2S = -rO1; %Reactant

```

```

rZnS = rO1; %Product
rH2O = 2*rO1; %Product
rZnCl2 = rO1; %Product

%Coolant Specs
U = 300; %W/m^2-K
Cp_c = 1.25; %J/g-K, Heat capacity of coolant at T = 600 C
A_s = 2 * L * pi() * (Do/2); %surface area that fluid is in contact
with

%Temperature Profile
%Reactor
ReactHeating = (rO1 * H_rO1); %J/L-hr
Cooling = (U * A_s * (T_Reactor-T_coolant)) * (60*60/
Volume_Reactor); %J/L-hr
HeatCap = (FZnO*cp_ZnO) + (FHCl*cp_HCl) + (FH2S*cp_H2S) +
(FZnS*cp_ZnS) + (FH2O*cp_H2O) + (FZnCl2*cp_ZnCl2); %kPa/m^3
dTrdV = (ReactHeating - Cooling)/HeatCap; %K/L

%Coolant Balance
dTcdV = (ReactHeating - Cooling)/ (m_c * Cp_c);%K/L

%%Pressure drop was ignored, but this was scratch work if process was
%%considered
%Pressure Drop Profile
% nu = (FZnO + FHCl + FH2S + FZnS + FH2O + FZnCl2)/(rho);%m^3/hr
% nus = nu/(60*60);%m^3/s
% dPdv = -(1-phi)*nu/ (Dp*phi^3*(A_c)^2) *((150*(1-phi)*mu/Dp) +
1.75*(rhov/A_c));%kPa/m^3
% dPdV = dPdv/1000; %kPa/L
% MW_ZnO = 81.38; % kg/kmol
% MW_HCl = 36.458; % kg/kmol
% MW_H2S = 34.1; % kg/kmol
% MW_ZnS = 32; % kg/kmol
% MW_H2O = 18; % kg/kmol
% MW_ZnCl2 = 136.286; % kg/kmol
%Pressure Drop Profile Constants
% phi = 0.28; %Void fraction = porosity
% mu = 20/1000/1000; %kPa-s, Constant at T=533 K, from HYSYS
% rhov = ((FZnO_in*MW_ZnO) + (FHCl_in*MW_HCl) + (FH2S_in*MW_H2S) +
(FZnS_in*MW_ZnS) + (FH2O_in*MW_H2O) + (FZnCl2_in*MW_ZnCl2))/(1000);
%kg/hr, mass flowrate, constant
% rho = 3020.52 * 1000; %g/m^3, I used the inlet flows
% %Inlet Flowrates
% FZnO_in = 2.35 * 1000; % mol/hr
% FHCl_in = 4.54 * 1000; % mol/hr
% FH2S_in = 0.0825 * 1000; % mol/hr
% FZnS_in = 0; % mol/hr
% FH2O_in = 0; % mol/hr
% FZnCl2_in = 0; % mol/hr

%Sends ODE solutions back to array for iteration
%dP = dPdV;

```

```
dFZnO = rZnO;  
dFHCl = rHCl;  
dFH2S = rH2S;  
dFZnS = rZnS;  
dFH2O = rH2O;  
dFZnCl2 = rZnCl2;  
dT_coolant = dTcdV;  
dT_Reactor = dTrdV;  
per_ode = [dFZnO; dFHCl; dFH2S; dFZnS; dFH2O; dFZnCl2; dT_coolant;  
          dT_Reactor];  
  
end
```

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Appendix H: Methanol Reactor Matlab Code

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`% Design Report Methanol Reactor Modeling`

Volume Domain

```
V_tot = 33609; % L
V_domain = [0 : 1 : V_tot]; % Integration domain
```

Initial Conditions

```
P_in = 8000; % Kpa
F_CO2_in = 4255 * 1000; % mol/hr .4255
F_H2_in = 18401.59 * 1000; % mol/hr
F_CO_in = 12206.02 * 1000; % mol/hr
F_H2O_in = 57.476 * 1000; % mol/hr
F_CH3OH_in = 235.83 * 1000; % mol/hr
F_N2_in = 1101.62 * 1000; % mol/hr
T_coolant_in = 400; % Kelvin WHAT SHOULD THIS TEMP BE
T_reactor_in = 543; % Kelvin
IC = [P_in F_CO2_in F_H2_in F_CO_in F_H2O_in F_CH3OH_in F_N2_in T_coolant_in
      T_reactor_in]; % Vector inlet conditions
```

Solve ODE

```
[Xsol, Ysol] = ode45('Design_methODE', V_domain, IC);
```

Data handling

Extracting solutions for each variable

```
P_sol = Ysol(:,1);
FCO2_sol = Ysol(:,2);
FH2_sol = Ysol(:,3);
FCO_sol = Ysol(:,4);
FH2O_sol = Ysol(:,5);
FCH3OH_sol = Ysol(:,6);
FN2_sol = Ysol(:,7);
T_coolant_sol = Ysol(:,8);
T_reactor_sol = Ysol(:,9);
```

Plotting

```
fig1 = figure(1);
set(fig1, 'Name', 'Pressure Drop');
area(Xsol, (P_sol)/100);
xlabel('Volume (L)');
ylabel('bar');
title('Pressure Drop');

fig2 = figure(2);
set(fig2, 'Name', 'Coolant Temperature');
area(Xsol, (T_coolant_sol));
xlabel('Volume (L)');
ylabel('Kelvin');
title('Coolant Temperature');

fig3 = figure(3);
set(fig3, 'Name', 'Methanol Flowrate');
area(Xsol, (FCH3OH_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('Methanol Flowrate');

fig4 = figure(4);
set(fig4, 'Name', 'H2 Flowrate');
area(Xsol, (FH2_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('H2 Flowrate');

fig5 = figure(5);
set(fig5, 'Name', 'H2O Flowrate');
area(Xsol, (FH2O_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('H2O Flowrate');

fig6 = figure(6);
set(fig6, 'Name', 'CO Flowrate');
area(Xsol, (FCO_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('CO Flowrate');

fig7 = figure(7);
set(fig7, 'Name', 'CO2 Flowrate');
area(Xsol, (FCO2_sol)/1000);
xlabel('Volume (L)');
ylabel('kmol/hr');
title('CO2 Flowrate');

fig8 = figure(8);
set(fig8, 'Name', 'Reactor Temperature');
```

```
area(Xsol, (T_reactor_sol));  
xlabel('Volume (L)');  
ylabel('Kelvin');  
title('Reactor Temperature');
```

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```
function [per_ode] = Design_methODE(X,Y)
```

Output Variables

```
P = Y(1);
FCO2 = Y(2);
FH2 = Y(3);
FCO = Y(4);
FH2O = Y(5);
FCH3OH = Y(6);
FN2 = Y(7);
T_coolant = Y(8);
T_reactor = Y(9);
```

Internal Variables

```
% Inlet Flow Rates -
% RATES CHECKED
F_CO2_in = 0.4255 * 1000; % mol/hr
F_H2_in = 18401.59 * 1000; % mol/hr
F_CO_in = 12206.02 * 1000; % mol/hr
F_H2O_in = 57.476 * 1000; % mol/hr
F_CH3OH_in = 235.83 * 1000; % mol/hr
F_N2_in = 1101.62 * 1000; % mol/hr

% Molar Constants CHECKED
MW_CO2 = 44.01; % g/mol
MW_H2 = 2.016; % g/mol
MW_CO = 28.01; % g/mol
MW_H2O = 18.02; % g/mol
MW_CH3OH = 32.04; % g/mol
MW_N2 = 28.013; % g/mol
Tot_moles = 32002.9615 * 1000; % mol/hr

% Heat Capacities CHECKED
cp_CO2 = 0.04558139091 * 1000; % J/mol-K
cp_H2 = 0.02908322993 * 1000; % J/mol-K
cp_CO = 0.03027465294 * 1000; % J/mol-K
cp_H2O = 0.03580121058 * 1000; % J/mol-K
cp_CH3OH = 0.06382141551 * 1000; % J/mol-K
cp_N2 = 0.02995442681 * 1000; % J/mol-K
```

```

% Coolant Coefficients
V_tot = 33609; % L - From Design_meth file
D = 0.0254; % m - From problem statement
Dp = 1 / 8 * D; % m - Heuristic
U = 300; % W/m^2-K - Constant assumption
v = 20; % Velocity of gas - arbitrary
Do = D + 0.006; % m - Outside diameter of tubes
rho = 16.68*1000; %g/m^3 - HYSYS
rhov =
((F_CO_in*MW_CO)+(F_CO2_in*MW_CO2)+(F_H2_in*MW_H2)+(F_H2O_in*MW_H2O)+(F_CH3OH_in*MW_CH3OH
(1000*60)); %kg/s - mass flowrate
vo = rhov/(rho/1000); %m^3/s
Ac_tube = pi*(D^2)/4; %m^2, Cross sectional area of a tube .00045
n = vo/(v*Ac_tube); %Number of tubes
Ac_tubes = Ac_tube*n; % m^2 Cross sectional area of all tubes
L = (V_tot/1000)/Ac_tubes; % m, Tube Length
As = 2 * pi * n * L * (Do / 2); % m^2, Surface area of all tubes
Cp_c = 2.25; %J/g-K, Heat capacity of coolant at T_max= 270 C= 543 K
m_c = 1000000000; %Somewhat arbitrary, g/hr
tau = (V_tot / 1000) / vo; % Space time (s)

% Heats of Reaction
H_r01 = 39.616 * 1000; % J/mol
H_r02 = -98.735 * 1000; % J/mol
H_r03 = -59.118 * 1000; % J/mol

% Pressure Drop Constants
phi = 0.41; % From Falk et al.
mu = 2.29*10^(-8); %kPa-s, Constant at avg reactor temp K, from HYSYS
R = 8.314; % J/mol-K

```

ODE Definitions

Partial Pressures

```

pCO2 = (FCO2 / (Tot_moles)) * P; %Kpa
pH2 = (FH2 / (Tot_moles)) * P; %Kpa
pCO = (FCO / (Tot_moles)) * P; %Kpa
pH2O = (FH2O / (Tot_moles)) * P; %Kpa
pCH3OH = (FCH3OH / (Tot_moles)); %Kpa
bpCO2 = pCO2 / 100; % bar
bpH2 = pH2 / 100; % bar
bpCO = pCO / 100; % bar
bpH2O = pH2O / 100; % bar
bpCH3OH = pCH3OH / 100; % bar

% B values
bCO2 = (7.05*10^(-7))*exp(61700/(R*T_reactor)); % bar-1 - Adsorbtion
coefficient
bCO = (2.16*10^(-5))*exp(46800/(R*T_reactor)); % bar-1 - Adsorbtion coefficient
bH = (6.37*10^(-9))*exp(84000/(R*T_reactor)); % bar-1/2 - Adsorbtion
coefficient

```

```

% Equilibrium values
K1 = 10^(5139/T_reactor - 12.621); % bar-2
K2 = 10^(-2073/T_reactor - 2.029); % unitless
K3 = 10^(3066/T_reactor - 10.592); % bar-2

% k Constants
k1 = (4.89*10^(7))*exp(-113000/(R*T_reactor));
k2 = (9.64*10^(6))*exp(-152900/(R*T_reactor));
k3 = (1.09*10^(5))*exp(-87500/(R*T_reactor));

% Reaction Rates
denom = (1 + bCO*bpCO + bCO2*bpCO2) * (bpH2^(1/2) + bH*bpH2O);
rO1 = ((k1*bCO)*((bpCO*bpH2^(3/2) - (bpCH3OH/(bpH2^(1/2)*K1))) / denom))*3600;
rO2 = ((k2*bCO2)*((bpCO2*bpH2 - (bpCO*bpH2O/K2))/denom))*3600;
rO3 = ((k3*bCO2)*((bpCO*bpH2^(3/2) - (bpCH3OH*bpH2O/(bpH2^(3/2)*K3))) /
denom))*3600;

% Species Material Balances
rCO2 = -rO2 - rO3;
rCH3OH = rO1 + rO3;
rH2 = -2*rO1 - rO2 - 3*rO3;
rCO = rO2 - rO1;
rH2O = rO2 + rO3;
rN2 = 0;

% Reactor Temperature Balance
R_heat = (rO1 * H_rO1) + (rO2 * H_rO2) + (rO3 * H_rO3); %J/L-hr
R_cool = (U * As * (T_reactor - T_coolant)) * (60 / V_tot); %J/L-hr
HeatCap = (FCO2*cp_CO2) + (FH2*cp_H2) + (FCO*cp_CO) + (FH2O*cp_H2O) +
(FCH3OH*cp_CH3OH);
dTrdV = (R_heat - R_cool) / HeatCap; %K/L

% Coolant Temperature Balance
dTcdV = (R_heat - R_cool) / (m_c * Cp_c); %K/L

% Pressure Drop
nu = ((FCO2*MW_CO2)+(FH2*MW_H2)+(FCO*MW_CO)+(FH2O*MW_H2O)+(FCH3OH*MW_CH3OH))/
(rho*n); % m^3/hr
nus= nu/(60); %m^3/s
dPdv = (((1-phi) * nus) / (Dp * (phi ^ 3) * (Ac_tubes ^ 2))) * ((150*(1-
phi)*mu/Dp)+(1.75*(rhoV/Ac_tubes))); %kPa/m^3
dPdv=dPdv/1000; %kPa/L

% Send ODE Solutions back to original array for iteration
dP = dPdv;
dFCO2 = rCO2;
dFH2 = rH2;
dFCO = rCO;
dFH2O = rH2O;
dFCH3OH = rCH3OH;
dFN2 = rN2;
dT_coolant = dTcdV;
dT_reactor = dTrdV;

```

```
per_ode = [dP; dFCO2; dFH2; dFCO; dFH2O; dFCH3OH; dFN2; dT_coolant;  
          dT_reactor];
```

```
end
```

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Appendix I: Separator Design Hand Calculations

Link to Appendix I:

https://docs.google.com/spreadsheets/d/1FzZUDIW4awKCjE3PveYT-kZh_fQPapWRgVmy9KaIRJI/edit?usp=share_link

Appendix J: Heat Exchanger Design Hand Calculations

Link to Appendix J:

https://docs.google.com/spreadsheets/d/1EA9430dVbHo-Pw-oOPslJdXqpMJEL2TJzuW1icQj_uc/edit?usp=share_link

Appendix K: Pumps and Compressors Hand Calculations

Link to Appendix K:

https://docs.google.com/spreadsheets/d/14eh_aYVlFFyHvyRVlrvmRDPwJHU0OpeHzdVAK9iOGr4/edit?usp=share_link

Appendix L: Heliostat Design Excel Calculations

Link to Appendix L:

https://drive.google.com/drive/folders/1nu7zNHpHOjIQ2UbOOXunBKH-fl46Dcep?usp=share_link

Appendix M: Aspen Energy Analyzer Heat Integration File

Link to Appendix M:

https://drive.google.com/file/d/1DOgb_FSOxraQQ6jlttshos2irpy9GLz/view?usp=share_link

Appendix N: Economics Excel File

Link to Appendix N:

https://drive.google.com/file/d/1i6PihEBqA7IO9OpMvUvbHZjZwie-cPrF/view?usp=share_link