DIMETHYL ETHER PROCESS

TSMT

OUR TEAM

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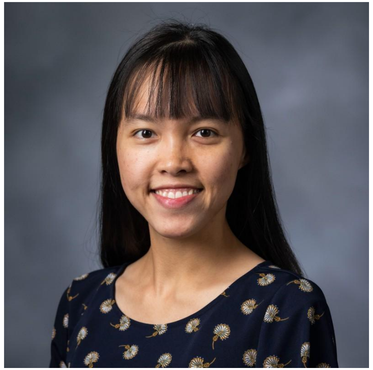


TRAN DIEP

Presentation Outline

INTRODUCTION
Background, key findings

SAFETY & ENVIRONMENT
Ethics and Societal Impacts

PROCESS
PFD, Reaction and Kinetics, Thermodynamics, Control

ECONOMICS
Costs and Profitability

PROJECT SCHEDULE
Future Work, Timeline, Recommendations

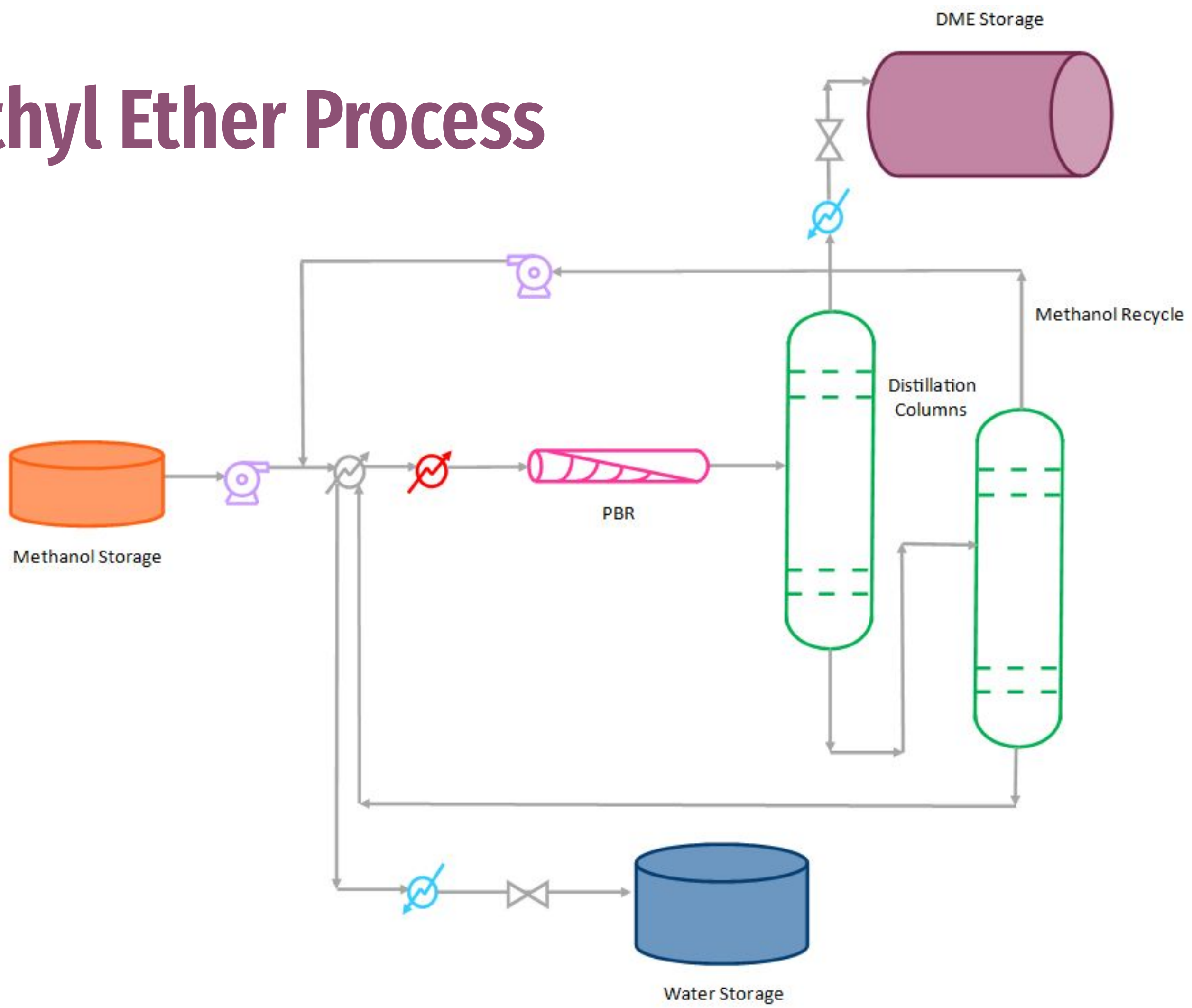
INTRODUCTION

Assignment: Complete preliminary design of dimethyl ether (DME) production

Goal: Produce at least 70,000 metric tons of DME/yr

- DME Usage: gasoline alternative or alternative to diesel fuel
- Global DME production rate increased from 7.80 million to 8.16 million metric tons from 2019-2021 and is expected to continue to grow [1]
- Safety was number one priority in design considerations and plant operators will be thoroughly trained
- Process will be implemented in Marlin, TX, away from communities and at atmospheric conditions
- To protect the environment, we will ensure that we meet the permit requirements with respect to discharging water into a nearby pond or lake
- The process we propose involves feeding pure methanol to a PBR reactor to convert the methanol to DME and water in which 2 distillation columns are used to separate the 3 components
- $4.56 million of cash flow/yr, NPV= $3.66 million, IRR= 17%

Dimethyl Ether Process



SAFETY & ENVIRONMENT

We are committed to designing inherently safe processes and protecting the environment at TSMT

- We are in compliance with all OSHA Process Safety Management regulations
- A HAZOP study will be done before pilot plant startup and adjusted before plant operation begins

- Chemicals Used
    - Methanol
        - Flammable liquid and vapor
        - Can be toxic in humans and animals if exposed
    - Dimethyl Ether
        - Very flammable gas, can explode if heated under pressure
        - Toxic in humans and animals
    - Water
        - Not flammable
        - No toxic effects in humans or animals unless contaminated

Safety (continued)
Risks and Management

Process Risks

- Hot temperatures coming into and out of the reactor and distillation columns
- High pressures throughout system
- Large quantities of methanol and DME

Mitigating Risks

- Pressure relief valves implemented throughout system
- Equipment will be grounded
- Controls system implemented
- Storage tanks kept and room temperature and pressure and away from ignition sources
- Storage vessels kept at room temperature and vapor pressure and away from ignition sources
- Maintenance will be performed regularly

Inherent Process Safety

1. **Intensification**: Only one week's supply of reactants and products stored in facility
2. **Substitution**: No replacement for methanol in this specific reaction
3. **Attenuation**: Using lowest recommended reactor temperature for reaction and lowest pressure possible to achieve good temperature profile in separation
4. **Containment**: Using equipment with good mechanical integrity
5. **Control**: Process designed to have minimal impact to workers, environment, and community should failure occur

Safety (continued)
Environment & Community Impact

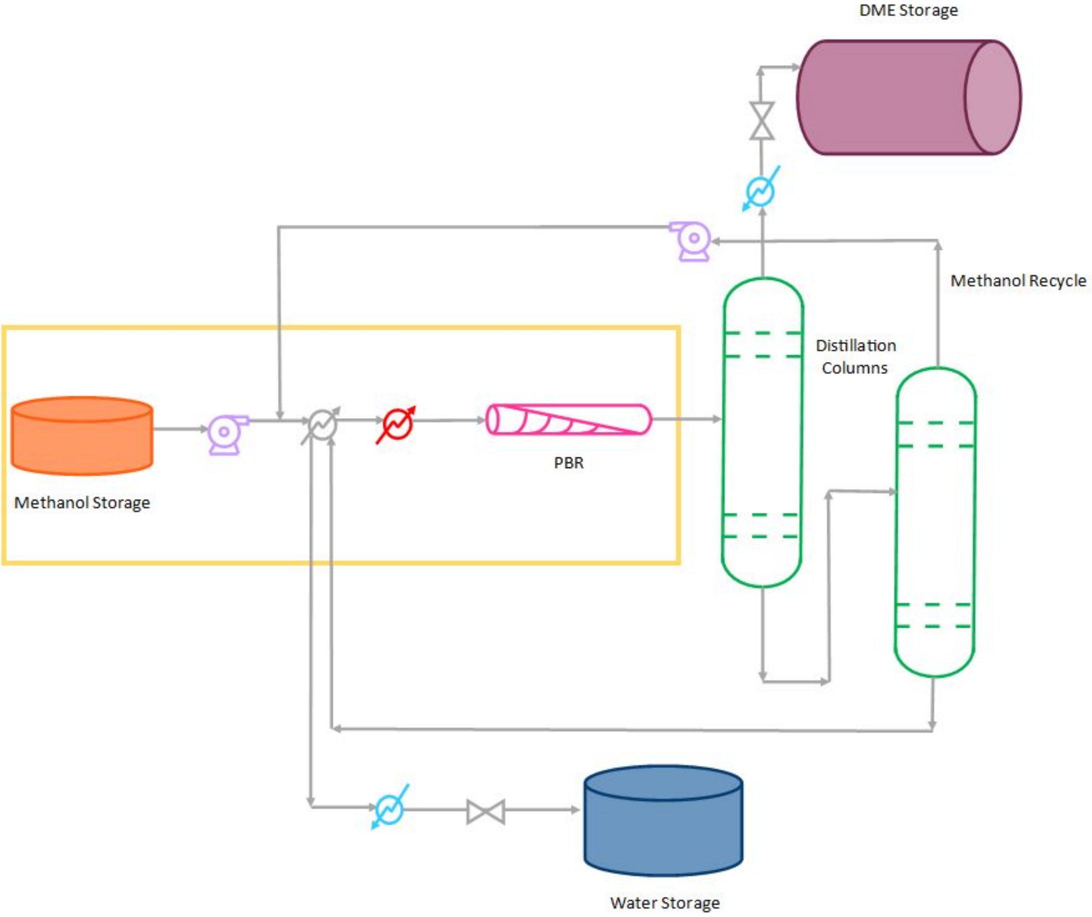
Environmental Measures

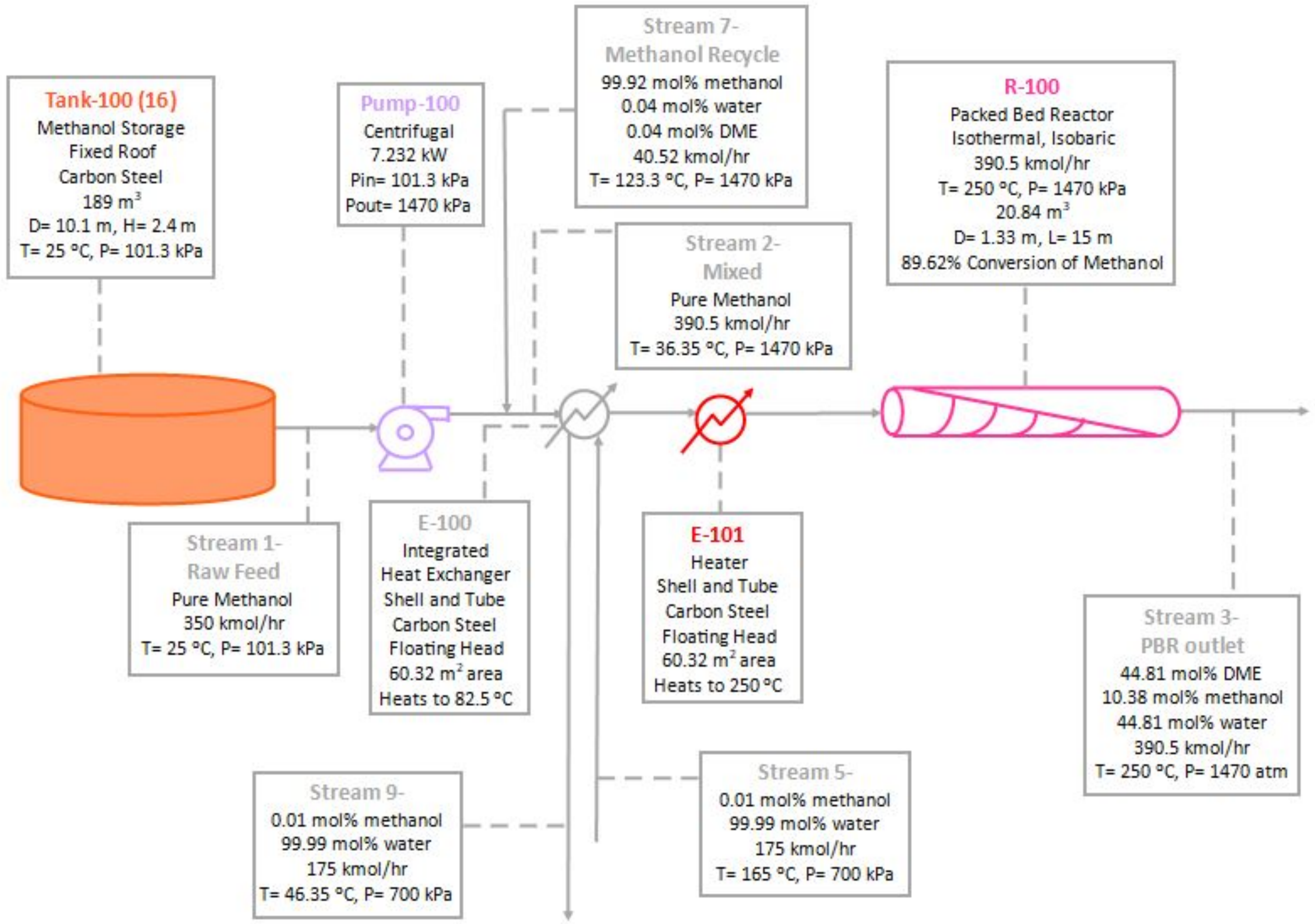
- Permit will be obtained to dispose of wastewater
- All Clean Water Act and Safe Drinking Water Act guidelines will be followed
- 177.3 mg methanol per L in wastewater

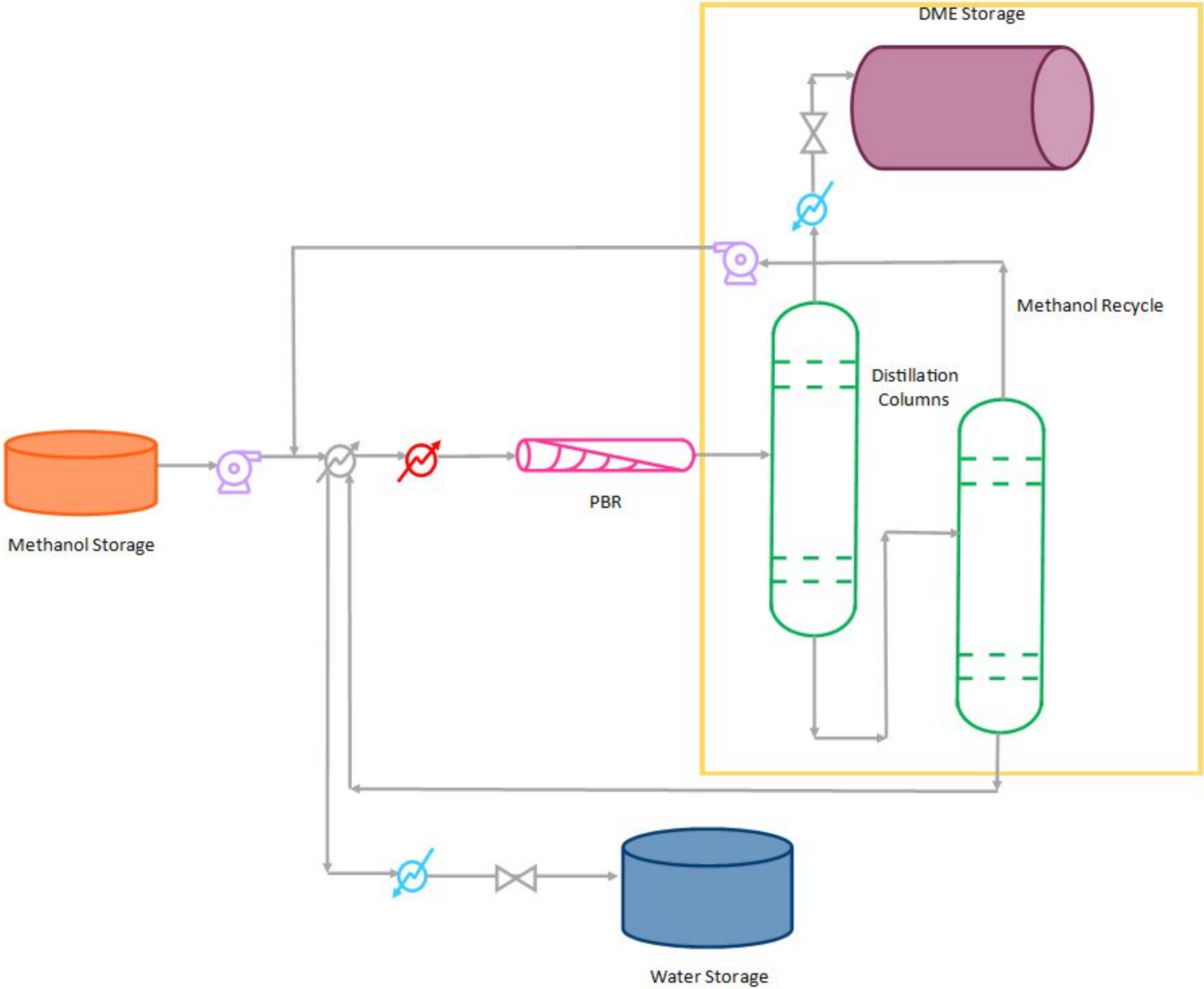
Community Impact

- Facility built away from residential areas
- New jobs created

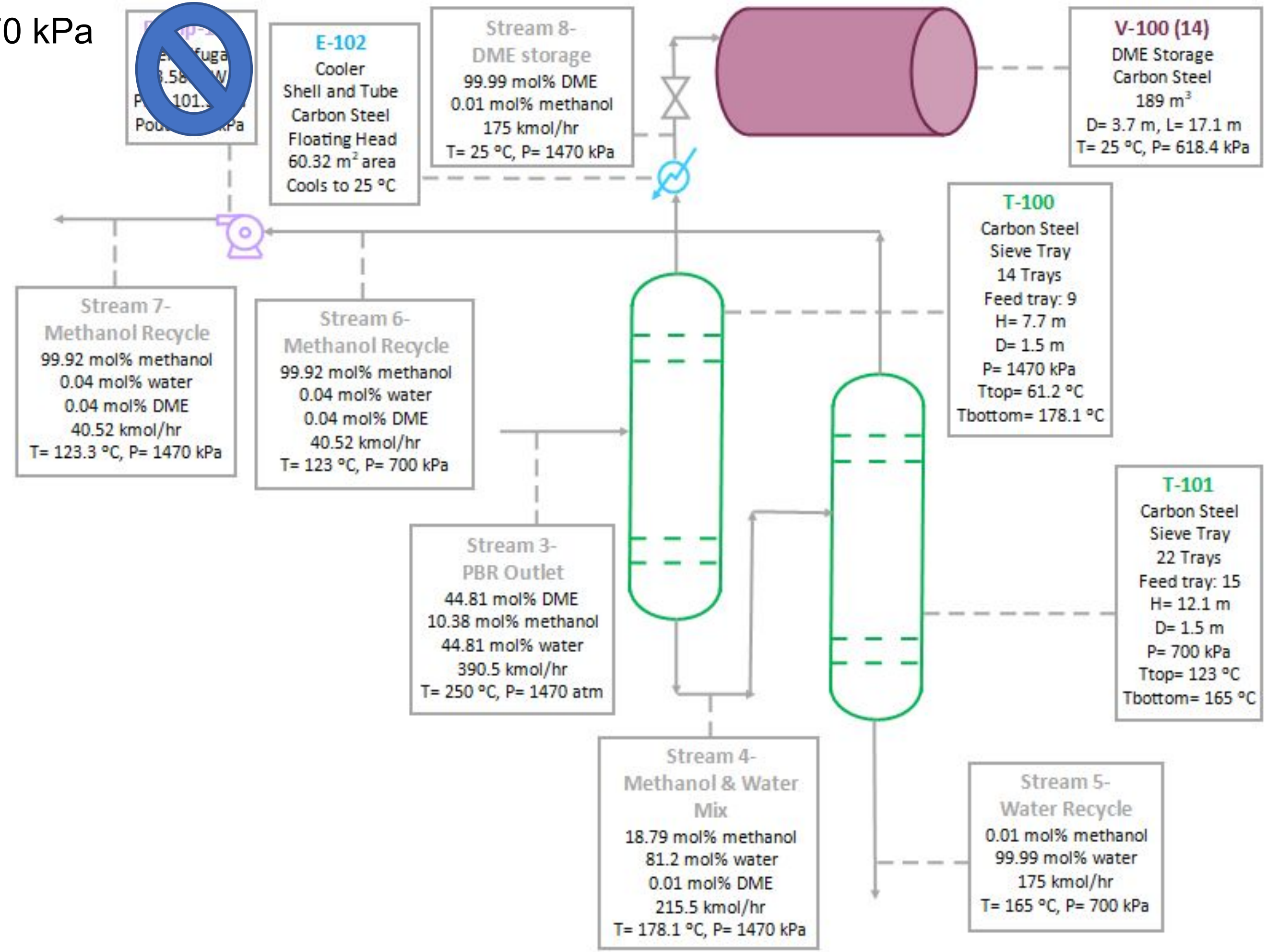
Process Walk Through

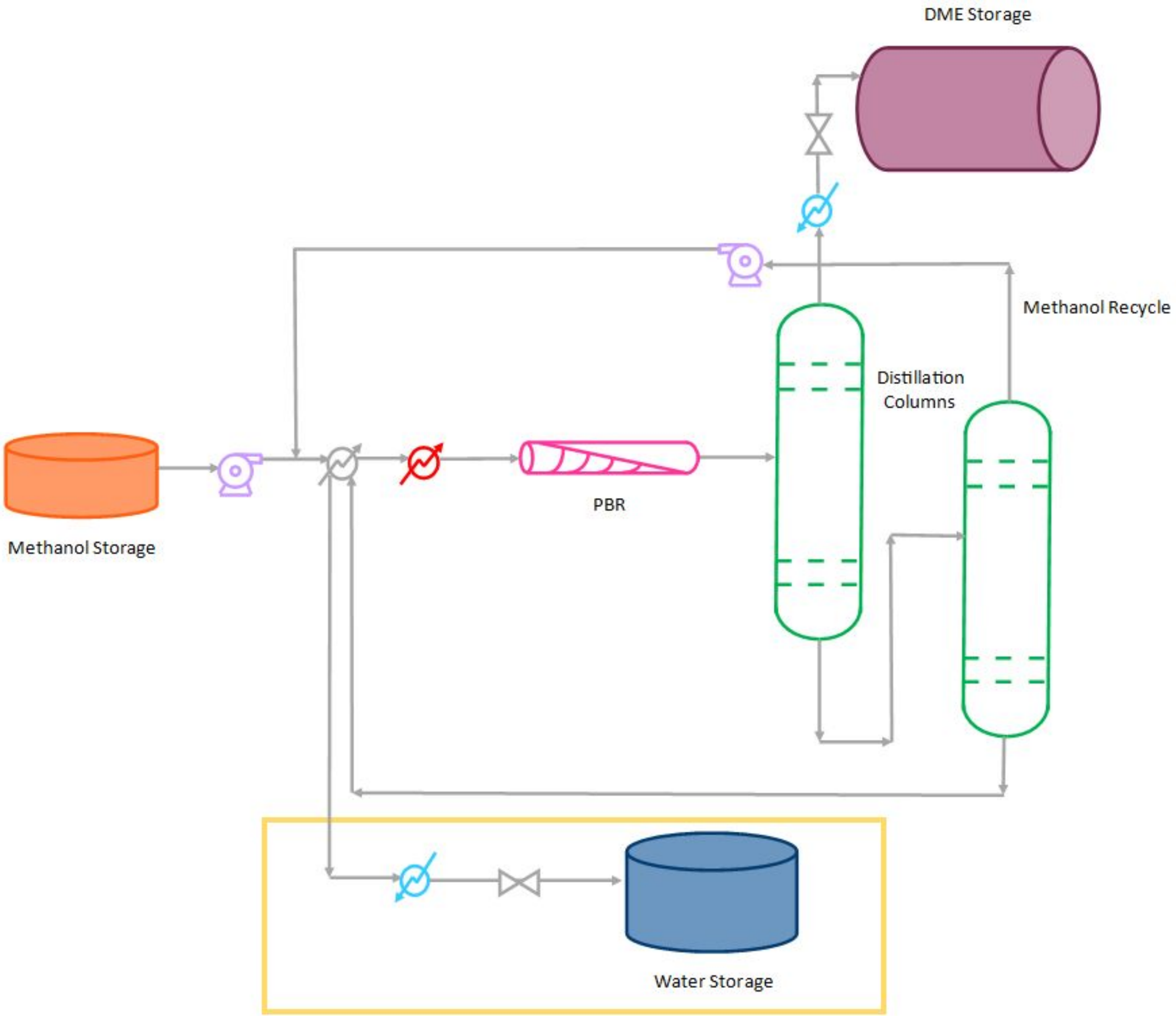


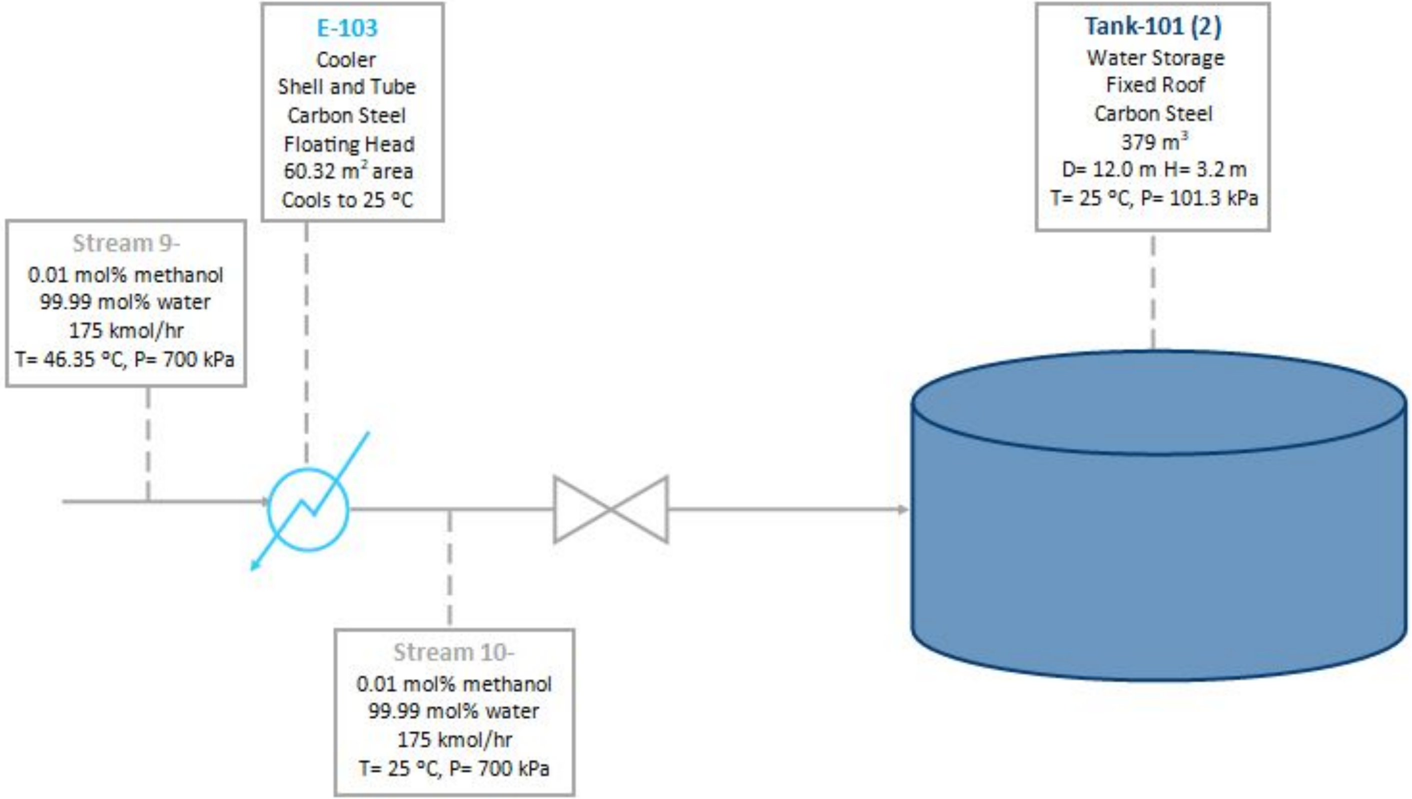

Tank-100 (16)
Methanol Storage
Fixed Roof
Carbon Steel
189 m³
D= 10.1 m, H= 2.4 m
T= 25 °C, P= 101.3 kPa
Pump-100
Centrifugal
7.232 kW
Pin= 101.3 kPa
Pout= 1470 kPa
Stream 7-
Methanol Recycle
99.92 mol% methanol
0.04 mol% water
0.04 mol% DME
40.52 kmol/hr
T= 123.3 °C, P= 1470 kPa
R-100
Packed Bed Reactor
Isothermal, Isobaric
390.5 kmol/hr
T= 250 °C, P= 1470 kPa
20.84 m³
D= 1.33 m, L= 15 m
89.62% Conversion of Methanol
Stream 2-
Mixed
Pure Methanol
390.5 kmol/hr
T= 36.35 °C, P= 1470 kPa
Stream 1-
Raw Feed
Pure Methanol
350 kmol/hr
T= 25 °C, P= 101.3 kPa
E-100
Integrated
Heat Exchanger
Shell and Tube
Carbon Steel
Floating Head
60.32 m² area
Heats to 82.5 °C
E-101
Heater
Shell and Tube
Carbon Steel
Floating Head
60.32 m² area
Heats to 250 °C
Stream 3-
PBR outlet
44.81 mol% DME
10.38 mol% methanol
44.81 mol% water
390.5 kmol/hr
T= 250 °C, P= 1470 atm
Stream 9-
0.01 mol% methanol
99.99 mol% water
175 kmol/hr
T= 46.35 °C, P= 700 kPa
Stream 5-
0.01 mol% methanol
99.99 mol% water
175 kmol/hr
T= 165 °C, P= 700 kPa


DME Storage
Methanol Recycle
Distillation
Columns
Methanol Storage
PBR
Water Storage

P_out = 1470 kPa
0.552 kW




DME Storage
Methanol Recycle
Distillation
Columns
Methanol Storage
PBR
Water Storage


E-103
Cooler
Shell and Tube
Carbon Steel
Floating Head
60.32 m² area
Cools to 25 °C
Tank-101 (2)
Water Storage
Fixed Roof
Carbon Steel
379 m³
D= 12.0 m H= 3.2 m
T= 25 °C, P= 101.3 kPa
Stream 9-
0.01 mol% methanol
99.99 mol% water
175 kmol/hr
T= 46.35 °C, P= 700 kPa
Stream 10-
0.01 mol% methanol
99.99 mol% water
175 kmol/hr
T= 25 °C, P= 700 kPa

REACTION AND KINETICS

Reaction:

$$2CH_3OH = \quad CH_3OCH_3 + H_2O$$

Rate Equation:

$$r = \frac{1.37x10^{10}\exp\frac{-2544}{RT}C_{CH_3OH}^2 - \frac{C_{(CH_3)_2O}C_{H_2O}}{K}}{\left(1 + 46.4x10^{-3}exp\frac{35280.5}{RT}C_{CH_3OH}^{0.5} + 84.7x10^{-3}exp\frac{42152}{RT}C_{H_2O}\right)^4}$$

$$K = 0.1103exp\frac{2708.6}{T}$$

Catalyst: Mordenite Zeolite

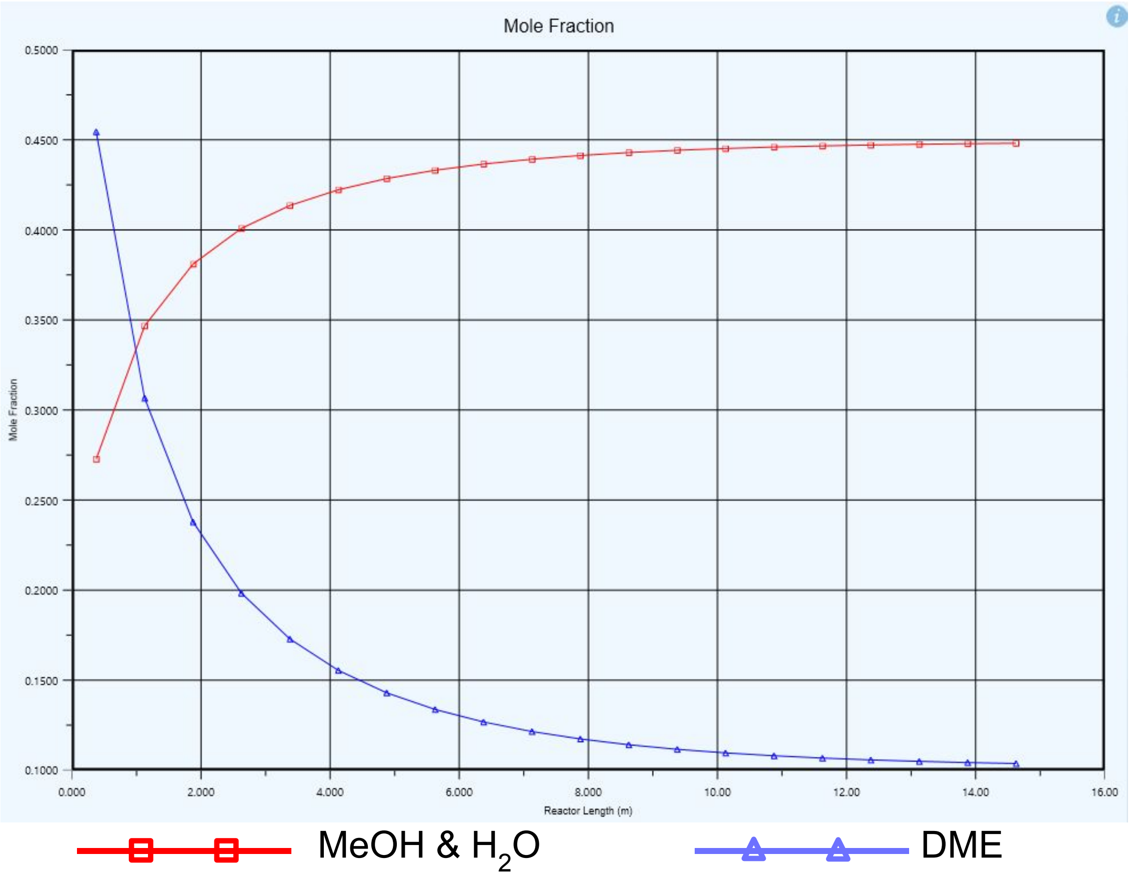
Reactor Specifications:

- PBR—can get the highest reaction rate at the highest concentration of methanol
- T = 250°C
- P = 1470 kPa
- Isothermal and isobaric
- Conversion Target = 90%
  - Irreversible Reaction
  - DME/Water liquid immiscibility when over 90% conversion

Reactor Control:

- Hot utility before reactor
- Temperature sensors along reactor
  - Monitor temperature and can adjust hot utility temperature
  - Safety
- Cooling utility to remove 3572 MJ/hr from reactor
- Pressure Relief Valve

REACTION AND KINETICS



HEAT INTEGRATION

Integrated heat exchanger specifics:

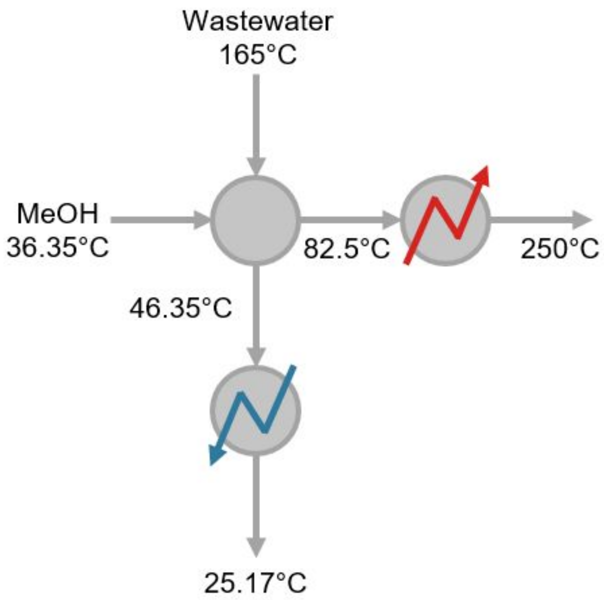
- Floating head, shell and tube configuration
- 1 shell pass, 2 tube passes per shell
- 60.32 m^2
- Carbon steel

Control:

- Implement temperature sensor on outlet MeOH stream that will change wastewater flowrate through heat exchanger

Start-up considerations:

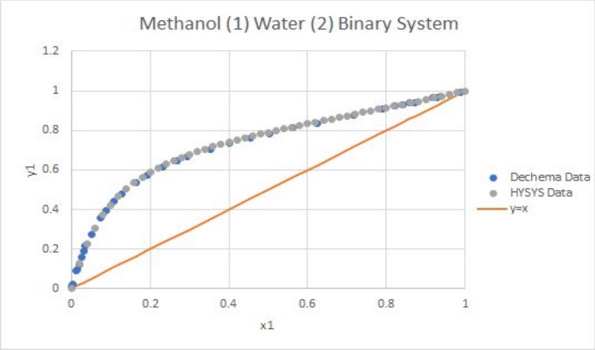
- Run hot utility to raise MeOH from 36.35°C to 250°C
- Once wastewater is produced, run through heat exchanger to achieve heat integration and lower heat utility as needed

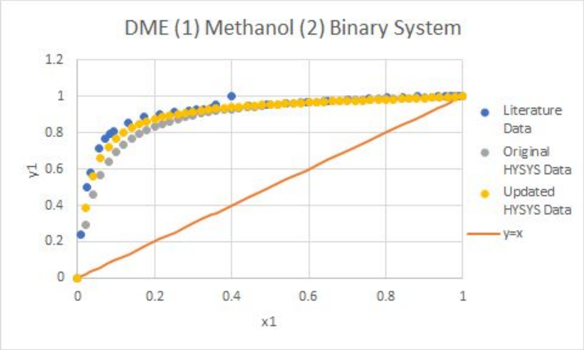


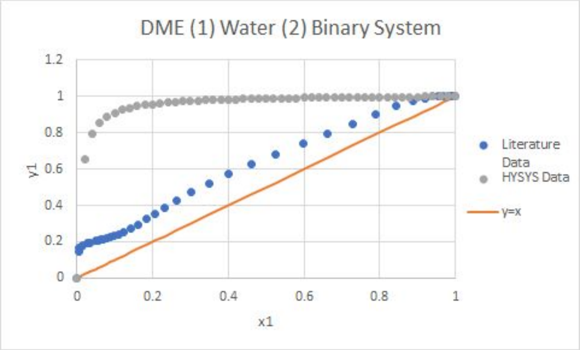
Stream	ṅ (kmol/h)	Cp_{avg} (kJ/kmol-K)	Q Unintegrated (kJ/h)	Utilities Q (kJ/h)	|Q| Saved with Integration (kJ/h)
MeOH	390.5	4.785E+04	1.231E+07	1.070E+07	1.603E+06
Wastewater	175.0	77.22	-1.890E+06	-2.780E+05	1.603E+06

THERMODYNAMICS

- Used NRTL equation since we are using polar compounds and it is good for modeling liquid nonidealities in a tertiary mixture as recommended by literature [2]
- Binary coefficients researched in literature and compared to coefficients generated by HYSYS
- Methanol/Water binary coefficients determined through DECHEMA
- Articles describing phase equilibria [3,4] used to find binary coefficients for DME/Methanol and DME/Water
- Binary coefficients in HYSYS adjusted to match parameters reported in literature for DME/Methanol
- HYSYS binary coefficients kept for DME/Water







COLUMN OPERATIONS AND CONTROL

Tower #	# of Stages	Feed Stage	Diameter (m)	Height (m)	Tray Space (m)
T-100	14	9	1.500	7.70	0.550
T-101	22	15	1.500	12.1	0.550

Operations and control strategy for both columns:

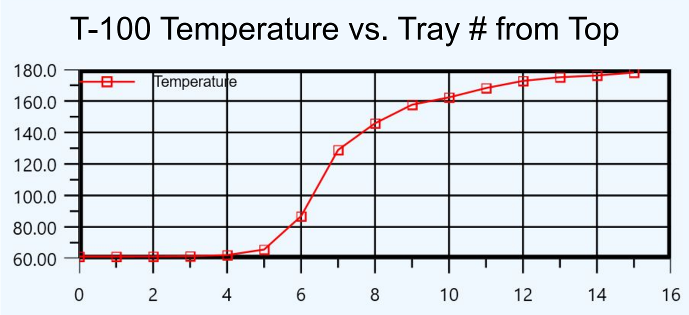
- Pressure sensors and control valves on reflux lines
- Level sensor, flow sensor, and control valve on distillate lines
- At least 1 temperature sensor at feed tray and control valve on reboiler utility stream
- Level sensor, flow sensor, and control valve on bottoms lines
- Current columns run on purity parameters; future work will change to controllable parameters

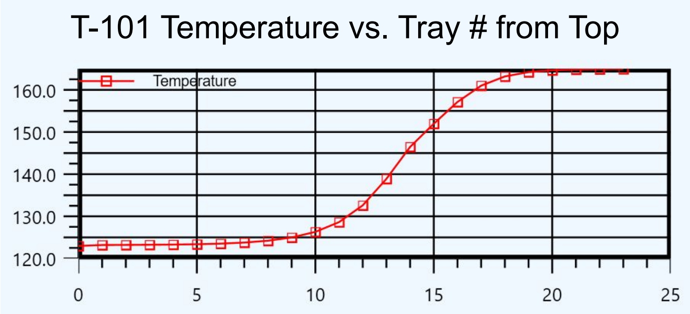
Start up

- Introduce feed; start reboiler then condenser
- Check temp. profiles before removing product
- Open valves on streams to allow build-up of momentum for pumps
- Add inert (i.e. N_2) to maintain pressure in vapor space if needed

Resilience

- HYSYS simulation overcompensates number of stages
- S-curve achieved with both columns
- Control system designed to prevent upsets





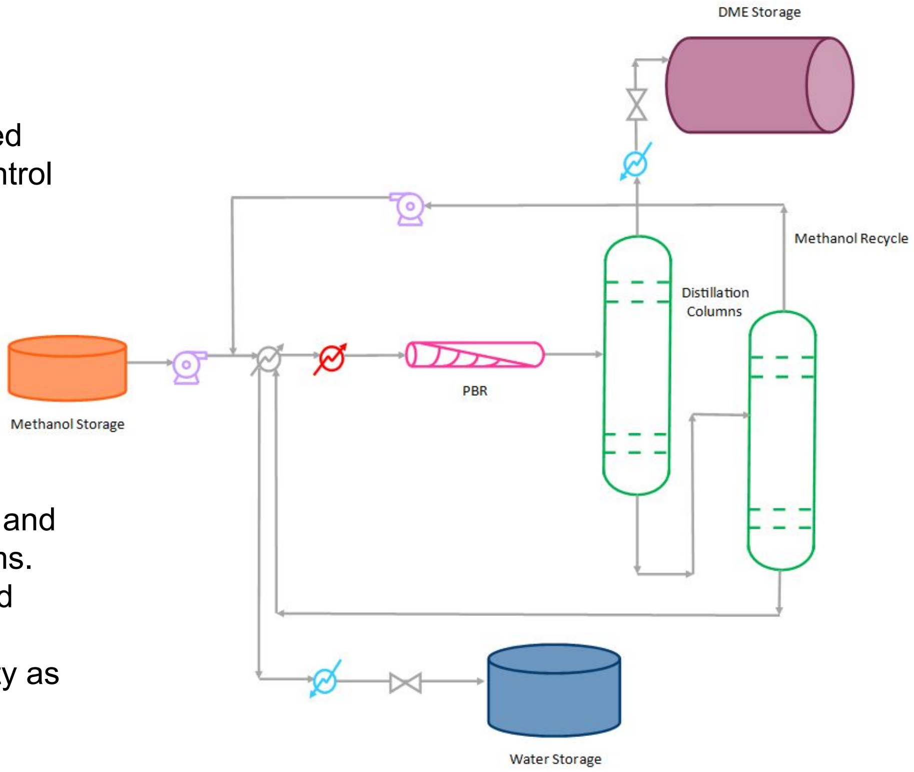
PROCESS SUMMARY

Results:
- 70,625 metric tons of DME product/year at 99.99wt% DME

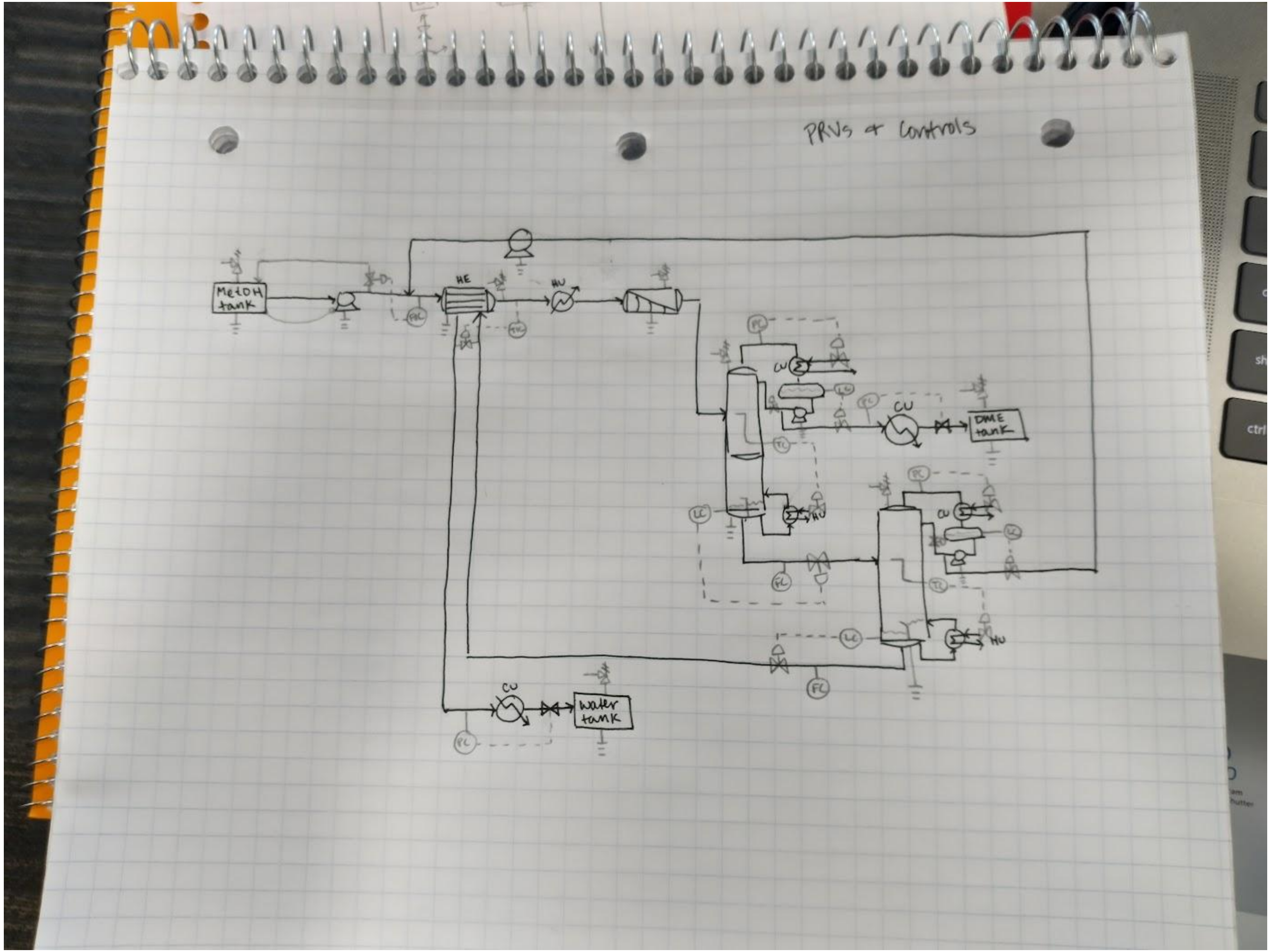
Quality of process design/reliability:
- Produce higher purities of DME, water, methanol than required
- Extra pump, 20% headspace in tanks/vessels, safety and control system implemented in final design

Start-up:
- Prepare the catalyst.
- Prime the pump for the methanol from storage.
- Use hot utility to heat up methanol at first and to maintain isothermal conditions in PBR.
- Let the methanol run through the reactor.
- Introduce feed to first column. Start reboiler, then condenser, and look at temperature profile. Check pressure of product streams. Introduce bottom stream of first column to second column and repeat on second column.
- Run wastewater through heat exchanger and reduce hot utility as needed.

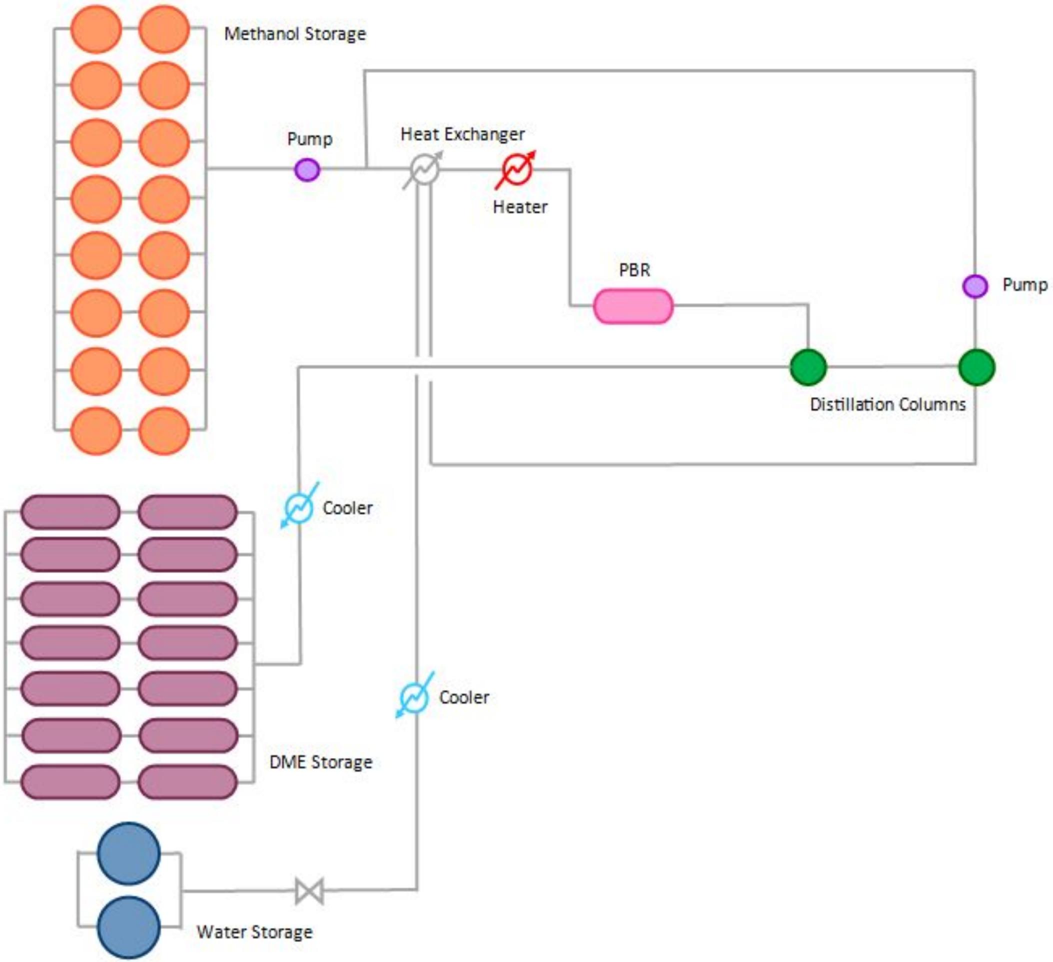
Resilience:
- Recommended preliminary safety and control system



Safety and Control System



PLANT LAYOUT



ECONOMICS

Capital Equipment	Quantity	Total Module Cost ($)
Reactor	1	169,000
Heat exchanger	1	173,000
Storage tank	18	2,460,000
Storage vessel	14	18,500,000
Distillation Columns	2	579,000
Heater	1	173,000
Cooler	2	343,000
Reboiler	2	59,000
Condenser	2	59,000
Pump	2 (+2 spare)	124,000
Total FCI		22,600,000

Capital	Cost ($)
FCI	**22,600,000**
Working Capital	**3,400,000**
Total	**26,000,000**

ECONOMICS

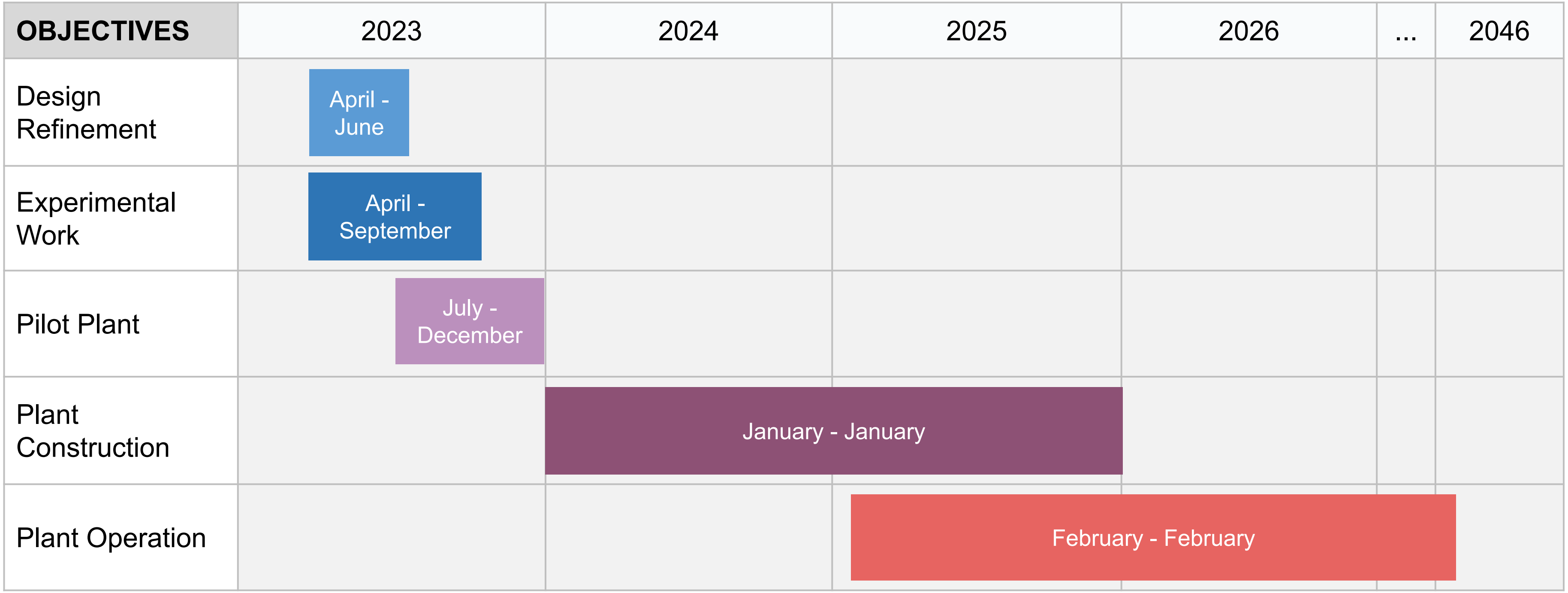
Operating time: 11.5 months/year

Item	Unit cost ($/kg)	Annual Total ($)
Raw Material (Methanol)	0.51	48,300,000
Wastewater Treatment	0.03	787,000
Utilities	N/A	861,000
Operating Labor	N/A	937,000
Product (DME)	1.12	75,100,000
Total Cost of Manufacturing		68,100,000

Parameters	
Depreciation	MACRS
Taxes	35%
Construction period	2 years
Plant life	20 years

Item	
Revenue	$75,100,000/r
Cash flow	**$4,560,000/yr**
NPV	**$3,660,000**
IRR	**17%**

FUTURE WORK – PROJECT TIMELINE



RECOMMENDATIONS

- **Design refinement:**
  - Pressure relief valves to be added on storage vessels, storage tanks, distillation columns, PBR, and heat exchangers with a possible phase change
  - Account for pressure drops across piping and pieces of equipment and add pumps/compressors where needed
  - Temperature control on reactor to be added to avoid deactivating the catalyst, controls (temperature, pressure, flow, and level) for the distillation column, backup pump

- **Experimental work:**
  - Determine the lifetime of the catalyst by monitoring the conversion of methanol over time
  - Measure liquid-liquid equilibrium data for water and DME
  - Determine the best way to remove the heat from the PBR

- **Pilot plant:**
  - Confirm the lifetime of the catalyst by monitoring the conversion of methanol over time
  - Determine if distillation columns have enough trays to achieve the separation needed

We recommend moving forward with this project

THANK YOU !

Works Cited

[1] SkyQuest Technology Consulting Pvt. Ltd. "Dimethyl Ether Market to Hit Sales of $8.92 Billion by 2028: India, Germany, and US Are the Largest Exporter of Dimethyl Ether: Skyquest Technology." *GlobeNewswire News Room*. SkyQuest Technology Consulting Pvt. Ltd., 09 Dec. 2022. Web. 1 Apr. 2023.

[2] Dimian, Alexandre C., Costin Sorin Bildea, and Anton A. Kiss. "10 – Dimethyl Ether." *Applications in Design and Simulation of Sustainable Chemical Processes* (2019): 363.

[3] Park, So-Jin, Kyu-Jin Han, and Jürgen Gmehling. "Isothermal Phase Equilibria and Excess Molar Enthalpies for Binary Systems with Dimethyl Ether at 323.15 K." *Journal of Chemical & Engineering Data* 52, no. 5 (2007a): 1814-1818.

[4] Park, So-Jin, Kyu-Jin Han, and Jürgen Gmehling. "Vapor−Liquid Equilibria and HE for Binary Systems of Dimethyl Ether (DME) with C1−C4 Alkan-1-Ols at 323.15 K and Liquid−Liquid Equilibria for Ternary System of DME + Methanol + Water at 313.15 K." *Journal of Chemical & Engineering Data* 52, no. 1 (2007b): 230-234.