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Production of Propylene by Bromination of Propane

To: Process Development Group, Alkyl Products Limited (APL)

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Subject: FEL-1 Techno-Economic Assessment of a New Technology Route for
                  Production of Propylene by Bromination of Propane

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Executive Summary

A conceptual process design and techno economic analysis was performed for the conversion of propane and bromine to produce 100 kta of propylene in Alkyl Products Limited Company. The primary feedstock is propane and bromine gas feed priced at \$200/MT and \$3,000/MT mixture respectively. The main product propylene is priced at \$900/MT.

The base case evaluation using 3 PFRs, 1 electrochemical reactor, and 6 distillation columns. The key design variable was optimized by maximizing the net present value (NPV), at which condition the process can provide \$63 MM/yr in gross chemical sales revenue. The finalized process design consumes 32.8 MJ energy and generates 1.5 kg CO_2 for every kilogram of propylene produced.

Fixed costs were dominated by capital recovery. TCI = \$169 MM, based on a 2 year construction time, an enterprise rate of 10%, after 13 years of operation the project NPV = \$18 MM, NPV% =0.69%, IRR = 12%.

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1 Introduction

The current global propylene market is estimated to be $3.67 billion. This market is projected to reach $5.66 billion by 2030 with a 4.5% compound annual growth during these years [1]. Propylene prices have grown substantially (9% since 2017) due to increasing crude oil price trend.

Using the abundance of cheap propane supply, Alkyl Products Limited has been taking advantage of producing propylene via the conventional technology route of thermal cracking of propane at 850°C and 3 bar pressure in a pyrolysis furnace. However, this route requires massive investment for propane-propylene splitters which are very large cryogenic distillation columns with a large number of stages and a large vapor rate. The Corporate R&D Department has been researching new chemical routes to produce propylene without these large propane-propylene splitters. The new routes include 5 reactions in 3 chemical sub-plants (See 1.1 Reaction Chemistry).

Accounting for the cost of the feedstock and selling potential of the product (Table 1), the maximum economic potential of the design suggested herein is approximately $65 MM/yr (See App. I.3 for economic potential calculations). This preliminary calculation highlights tight profit margins when finalizing a design with a desirable return on investment.

Table 1. Process chemical values for economic estimations.

Chemical Species	Price
Polymer-Grade Propylene (C_3H_6)	$900/MT
Pure Propane (C_3H_8)	$200/MT
Pure Hydrogen (H_2)	$1400/MT
Bromine (Br_2)	$3000/MT
CO_2 Charge	$75/MT
Fuel	$4.25 /GJ

1.1 Reaction Chemistry

Propane participates in the reaction with bromine gas (Br2) to produce n-bromopropane and hydrobromic acid (HBr) in Sub-Plant 1. However, n-bromopropane also reacts with bromine to produce the undesired by-product dibromopropane simultaneously. Dibromopropane can be hydrogenated back to n-bromopropane in a separate catalytic reaction. The bromopropane is catalytically dehydrobromination to produce propylene and HBr in Sub-Plant 2. A key step in this chemical route is to recover all the bromine tied up in HBr to produce bromine liquid and hydrogen gas in an electrochemical reactor in Sub-Plant 3.

The heat of reaction for the reactions in the 3 sub-plants are listed in Table 2. The data indicate that the propylene production reaction from n-bromopropane is endothermic. See appendices A and B for detailed material property, kinetic data, operating conditions, and catalyst use, respectively.

Table 2. Propylene production reactions with associated heat of reaction, at base-case operating conditions [15].

Sub-Plant	Reaction	ΔH_{rxn}, $[kJ/gmol]$
1	$C_3H_8 + Br_2 \rightarrow C_3H_7Br + HBr$	-61
1	$C_3H_7Br + Br_2 \rightarrow C_3H_6Br_2 + HBr$	+21
1'	$C_3H_6Br_2 + H_2 \rightarrow C_3H_7Br + HBr$	-94
2	$C_3H_7Br \rightleftharpoons C_3H_6 + HBr$	+113
3	$2HBr \rightarrow H_2 + Br_2$	+73

2 Process Design

2.1 Process Flow Diagram

Figure 1 on the following page depicts the process flow diagram used in the FEL-1 techno-economic evaluation of the propylene production process. Through this design, it is theoretically possible to produce 100 kta of 99.5 wt% propylene. Critical design choices include using three PFRs, one electrochemical cell, six distillation columns, and two recycle loops.
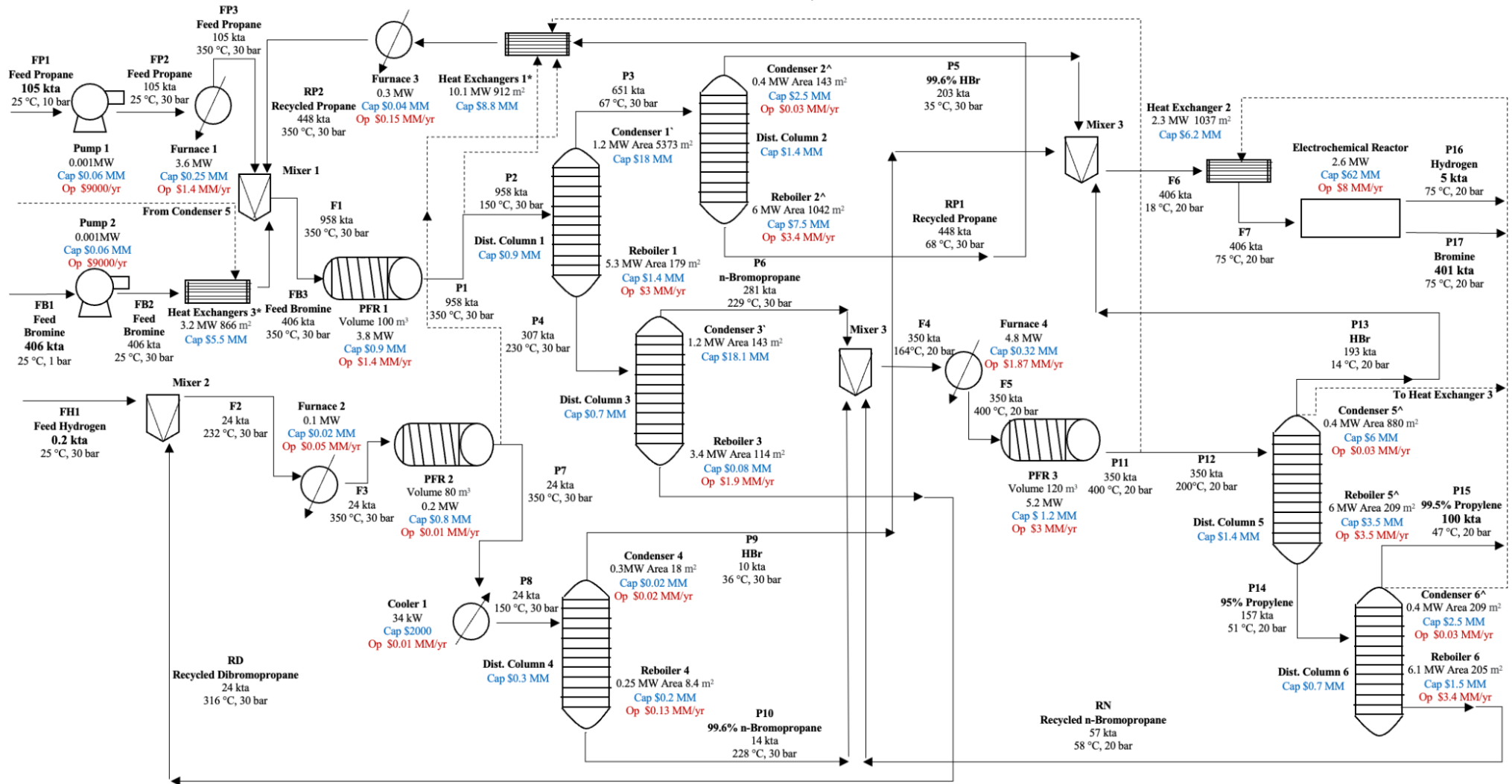
Total ISBL = $62 MM

Figure 1. Process flow diagram with labeled stream temperatures, pressures, and flow rates for base-case conceptual Propylene Production by Bromination of Propane process. (* means an heat exchanger system, ' means a reboiler or a condenser with no extra heating fluid used , ^ means a reboiler or a condenser with at least one extra heat exchange)

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2.2 Reactor Design

The first step in developing a conceptual process design is selecting the reactors that best suit the process of interest. The kinetic data acquired from the Corporate R&D Department reveal that the reactions in the first two sub-plants are in the gas phase, which indicates that plug-flow reactors (PFR) are more efficient than CSTRs for the same volume. Also, PFRs require low operating costs (labor cost), and they can run in a high conversion per unit volume. For these reasons, the 3 PFRs are used in this process. In sub-plant 3, an electrochemical reactor is used based on the electrode information provided by the Corporate R&D Department (See detailed sub-plant division and mole balances and in App. C & D).

In addition to the kinetic data developed by the R&D department, several variables are specified to run the whole design system and achieve 100kta of propylene production. As propane bromination is a radical reaction, the corresponding reaction conversion is assumed to be 1. The conversion of electrochemical reactors is also assumed to be 1. There are another 5 unknown variables for the PFR reactors: reaction temperature and propane-to-bromine molar ratio in sub-plant 1, dibromopropane conversion and hydrogen-to-dibromopropane molar ratio in sub-plant 1', n-bromopropane conversion in sub-plant 2. In this assessment report, the process development team chooses to fix the variables in sub-plant 1' and sub-plant 2. The optimization of the design was based on the Net Present Value (NPV) calculations (See App. E) by only varying the two variables in sub-plant 1.
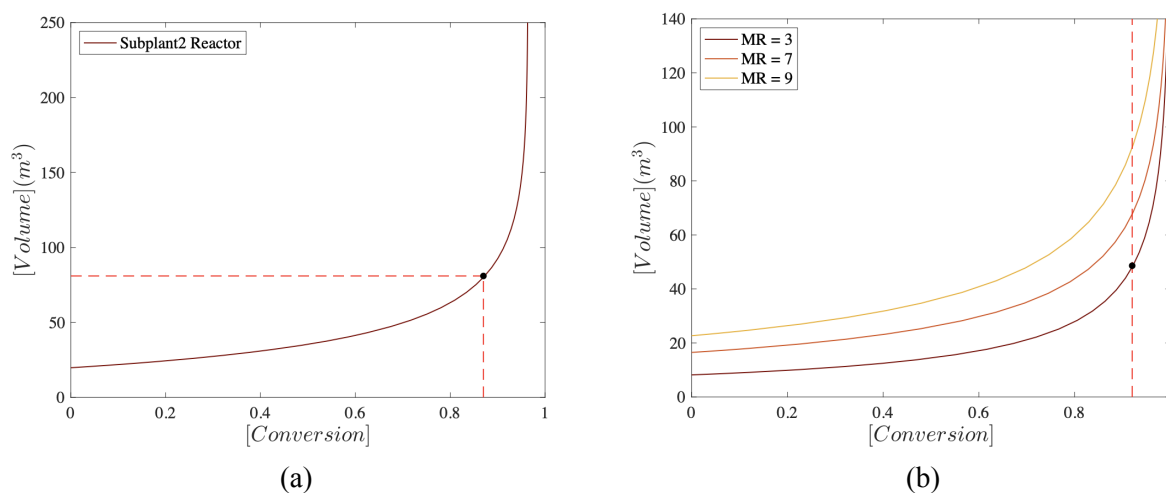

(a) (b)

Figure 2. (a) Volume of sub-plant 2 PFR reactor as a function of overall n-bromopropane conversion across the reactor. Curve is generated at 400°C and 20 bar. (b) Volume of sub-plant 1' PFR reactor as a function of overall dibromopropane conversion across the reactor. Curves are generated at 350°C and 30 bar at 3 different hydrogen to dibromopropane molar ratios: MR=3, MR=7, MR=9.

The principle for picking the fixed values for variables in sub-plant 1' and sub-plant 2 is approaching higher conversion as possible but before the reactor volume greatly increases. Based on the trend found in Figure 2a, the n-bromopropane conversion in sub-plant 2 is determined as 0.88. The trend in Figue 2b shows that at the same dibromopropane conversion, lower hydrogen-to-dibromopropane molar ratio results in a smaller reactor volume. The lower molar ratio will also reduce the cost for the separation of hydrogen recycle streams. Based on these analyses, the hydrogen-to-dibromopropane ratio in sub-plant 1' is determined as MR=3; the dibromopropane conversion in sub-plant 1' is determined as 0.92.

The remaining two variables, the molar ratio of propane-to-bromine at the inlet and the operating temperature of the reactor in Sub-Plant 1 will be the two design variables in the optimization of this design. Both of these two variables will affect the selectivity of n-bromopropane in PFR 1 and the capital cost of the corresponding equipment. The optimization of these variables finally determines the propane-to-bromine molar ratio to be 3:1, and the operating temperature of 350°C. Detailed optimization calculations are in the economic section of the report.

Table 3 summarizes the Sub-Plant 1, 1' and 2 reactor choices and their operating conditions used in this FEL-1 techno-economic evaluation. The selected operating temperature and pressures ensure the similar conditions to those used in the provided kinetic data. Solid Titanium is used as the reactor material of pricing, but the reactor requires a more corrosion resistant material (See safety considerations section). All three PFRs have conversions around 90%, which meets the technical data provided by the R&D department (See App. A). Also, the third PFR has a large volume, which sustains a high temperature of 400°C and produces the desired 100 kta propylene products.

Table 3. Reactor operating conditions and construction materials chosen for propylene production conceptual design.
*For pricing purposes only; this is not the actual material (See details in safety consideration section).
^PFR 1 propane-to-bromine feed ratio is 3:1 and PFR 2 hydrogen-to-dibromopropane feed ratio is 3:1.

Reactor	Pressure (bar)	Temp. (℃)	Fractional Conversion (%)	Feed Ratio	Volume (m^3)	Material
PFR 1	30	350	99.5	3:1^	100	Solid Titanium*
PFR 2	30	350	92	3:1^	80	Solid Titanium*
PFR 3	20	400	88	-	120	Solid Titanium*

To optimize the electrochemical reactor design, the primary design variable is the voltage used in the reactor power supply. Varying the voltage changes the surface area of the reactor, which is correlated with the reactor capital cost. Also, the change of voltage leads to the variations of power needed for the reactor, and the power can be used to calculate the reactor operating cost. The current-density vs. voltage data acquired by the Corporate R&D Department reveal that the minimum voltage requirement is 1.18 V, and the reactor also requires a minimum current of 15 billion A /yr to operate (see App. J).
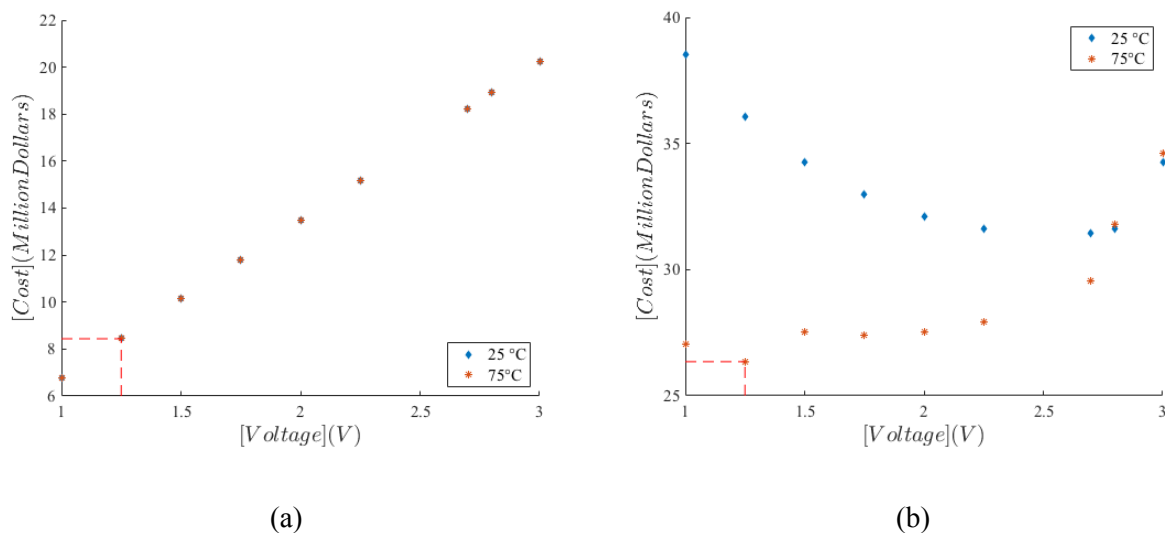
(a)   (b)

Figure 3. (a) Operating cost of the electrochemical reactor under different voltages and temperatures (b) Capital cost of reactor at different voltages and temperatures. Operating voltage at 1.25 V is shown in orange line

Based on the trends found in Figure 3, the operating conditions under 1.25V and 75°C provide the most optimal costs. Under these conditions, the total capital cost is $26 million and total operating cost is $8.44 million. Bromine will be collected as a gas after the reaction, which will then be dried using a solid drying agent, such as sodium sulfide.

2.3 Distillation Design

To optimize the distillation design, both direct and indirect split orders were considered. The distillation MATLAB design procedures assumed "constant molar flow" (CMO), that is, the latent heat of vaporization is independent of the mixture composition. Also, the assumption of a saturated liquid feed was made. [2] A lower vapor rate results in better performance of the distillation columns because if the distillation is conducted too rapidly, liquid-vapor equilibria will not be established in the fractionating column, leading to a poor separation of the compounds. From MATLAB calculations, the distillation vapor rates of the direct split order resulted in a lower value than indirect split orders (~30% less) (See detailed distillation calculations in App. I.2). As a result, a direct split order was performed.

Table 4 summarizes the operating conditions and the construction pricing materials used in this plant design. Distillation column 2, 3, and 6 have more than 50 stages to distillate and separate the chemical mixtures because the mixtures with a small difference in boiling points are fed into these columns (See boiling point details in App. A). Column 2 feed stream contains 74 mol% of propane and 26 mol% of HBr, with the composition of HBr at top up to 99.6% and the composition of recycled propane at bottom up to 94%. Column 3 feed stream contains 95 mol% of n-bromopropane and 5 mol% of dibromopropane, with the composition of n-bromopropane at top up to 100% and the composition of recycled dibromopropane at bottom up to 99.7%. Column 6 feed stream contains 95 mol% of propylene, 3 mol% of n-bromopropane and 2 mol% of dibromopropane, with the composition of propylene product at top up to 99.5% and the composition of recycled n-bromopropane at bottom up to 99%.

Column 5 has an extremely high reflux ratio to ensure the high purity (99.9%) HBr product is fed into the electrochemical reactor with a low temperature to meet the electrochemical reaction operating conditions (See details in App. A). Column 4 has a much smaller reboiler duty than other columns because the stream flow is small for the reboiler to generate the vapor supplied to the bottom tray of this column.

Table 4. Operating conditions and construction materials for distillation columns used in conceptual design of propylene production process by bromination of propane. The height was calculated assuming a stage spacing of 0.55 m.
*For pricing purposes only, not the the actual material (See details in safety considerations section)

Distillation Column	Pressure (bar)	No. Stages & Feed Stage	Height (m)	Reboiler Duty (MW)	Condenser Duty (MW)	Reflux Ratio	Material
1	30	20 & 4	14	5.3	1.2	2	Solid Titanium*
2	30	55 & 19	34	6	0.4	8.7	Solid Titanium*
3	30	52 & 20	31	3.4	1.2	2.3	Solid Titanium*
4	30	30 & 10	20	0.25	0.3	5	Solid Titanium*
5	20	40 & 19	26	6	0.4	21	Solid Titanium*
6	20	60 & 22	37	6.1	0.4	3.2	Solid Titanium*

2.4 Heating System Design

To optimize the heating system design, a heat integration analysis was generated. Four factors in the system were considered: capital costs, heating costs, efficiency, and overall carbon footprint. A pinch analysis performed in the HYSYS conceptual design (See details in App. F) by the process development team reveals that excluding the reboilers and condensers, the total amount of heating required by the process is around 28 MW, and the cooling is around 13 MW (See details in App. G). This design has a significant heating deficit of 14 MW in a total trim case. Further heat integration around condensers and heat exchangers were considered to decrease carbon emissions and the heating demand of this plant. The considerations saved 60 MW of energy in the whole design system. Table 5 shows the total heating and cooling parameters in the design system, including temperature changes and power changes.

Table 5. Heating system overview (Excluding the reactors, and continued in the next page).

System Type	dT (°C)	dH (kW)
Heating	381.1	67048
Cooling	-374	-60707

To optimize the heating system, the single cooler is needed to operate the cooling water at 12 °C in the condenser of distillation column 4. The temperature difference between condensers and reboilers in the distillation columns is 20°C, with the exception for column 4, which has a difference of 40°C. The energy use in this design is calculated as 32.8 MJ per kilogram of propylene product produced. Units that contain bromine and hydrogen were cost at a premium because of non-corrosive metal material usage. This prevents the embrittlement of the heat exchangers/furnaces (See details in the safety consideration section). For this reason, the price of titanium on titanium was used in estimating the capital costs.

This finalized heating system design is both carbon-dioxide emission intensive and water intensive. It produces 1.4 kta of carbon dioxide per kta of the propylene product. Therefore, significant investment in carbon capture or a supplementary renewable energy source is suggested for this process. The process also uses 0.98 kta of steam and 0.78 kta of cooling water. Furthermore, the process requires 1 MT of DowTerm A® to reach the temperature needed by reboilers in distillation column 1 and 3 (See more details under App. G).

3 Techno-Economic Analysis

3.1 Overall Capital Cost And Profits

The summarized results from the FEL-1 techno-economic analysis of a 100 kta propylene production plant are outlined in Table 6 and 7. In this analysis, the start-up costs are assumed to be 10% of the fixed capital cost, the working capital is assumed to be 10% of the fixed capital cost. The whole plant is assumed to have a 2-year construction period and a 13-year plant life. The fixed capital cost will be charged 50% each at the end of year 1 and 2, and there will be a salvage of 5% FCI returned back at the end of the plant life in year 15 (See App. H).

Table 6. Total capital investment for base-case conceptual design of bromination process.

Category	Cost (MM $)
Fixed Capital Investment, FCI	141
Start-up Costs, SU	14
Working Capital, WC	14
Total Capital Investment, TCI	$169 MM

Table 7. Profitability values for base-case conceptual design of bromination process.

Profitability Metric	Value
Net Present Value, NPV	$18 MM
Percent Net Present Value, NPV%	0.69 %
Internal Rate of Return, IRR	12.04 %
Revenue, R	$65 MM/yr

3.2 Optimization of Key Design Variables

The optimization of design variables is based on NPV analysis (see App. E). The catalysts are assumed to be replaced every 3 years. Equipments take a 10-year linear depreciation schedule. The total taxation rate is 27%, and the enterprise rate is assumed to be 10% annually.

It is observed that varying the two key design variables, the reactor temperature and propane to bromine molar ratio in sub-plant 1, the n-bromopropane selectivity and the PFR reactor volume in sub-plant 1 will change. This will further change the stream flow rates and the duty of corresponding equipment. Based on this analysis, it is expected that equipment capital costs will vary when design variables are picked at different values. It is also observed that changing the value of key design variables has nearly no effect on the inlet and outlet streams flow rates to the whole plant's system boundary. This means that the economic potential will not be affected by varying the design variables.

Therefore, in this optimization analysis, propane-to-bromine molar ratio was picked at MR=3, 5, 7 and reactor temperature was picked at 325°C, 350°C, 400°C, 450°C at each molar ratio; a total of 12 cases were compared for their NPV to determine the optimal values for the two design variables[1].

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[1] At the stage of optimizing NPV, utility cost was only estimated at its maximum value without energy integration,so the NPV is only rough estimation and not accurate enough. Once the optimal values for design variables are determined, NPV will be recalculated with heat integration to minimize the operating cost.
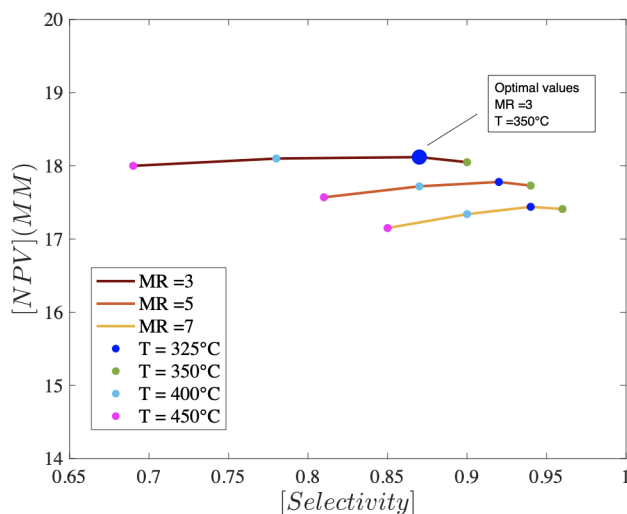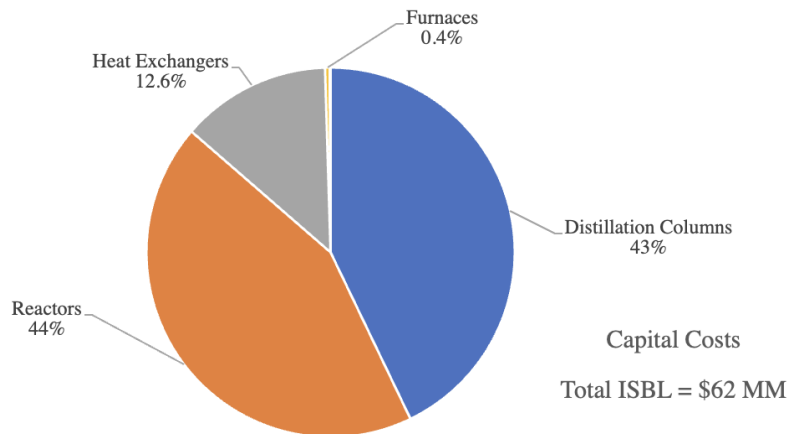
Figure 4. Conceptual design optimization of NPV as a function of selectivity of n-bromopropane in sub-plant 1 PFR reactor. Each selectivity has its corresponding temperature and molar ratio, marked and labeled in the legends.

Based on the trend found in Figure 4, the optimal values for the key design variables are determined to be T=350°C and propane-to-bromine MR =3 as these two variable values give the maximum NPV. The corresponding n-bromopropane selectivity is 0.87. These optimal values indicate that a reactor temperature higher than 350°C may bring heavy duty requirements to the equipment around the reactor, which will significantly increase the capital cost. A high propane-to-bromine molar ratio will increase the amount of propane needed to be separated in the distillation system, which will also increase the capital cost. After the values are determined, the equipment are repriced at the new reactor conditions.

Table 8. Installation and operating costs for equipment needed in base-case conceptual design of propylene production by bromination of propane.

Equipment	Installation Cost (MM $)	Operating Cost (MM $/yr)
Distillation Columns	26.7	15.4
Reactors	27.1	12.4
Heat Exchangers	8.2	-
Furnaces	0.25	3.5
Cooler	8×10^{-4}	0.01
Pumps	0.05	0.02
Total	$62 MM	$31 MM

Furnaces
0.4%

Heat Exchangers
12.6%

Distillation Columns
43%

Reactors
44%

Capital Costs

Total ISBL = $62 MM

(a)

Furnaces
11%

Distillation Columns
49%

Reactors
40%

Operating Costs

Total = $31 MM/yr
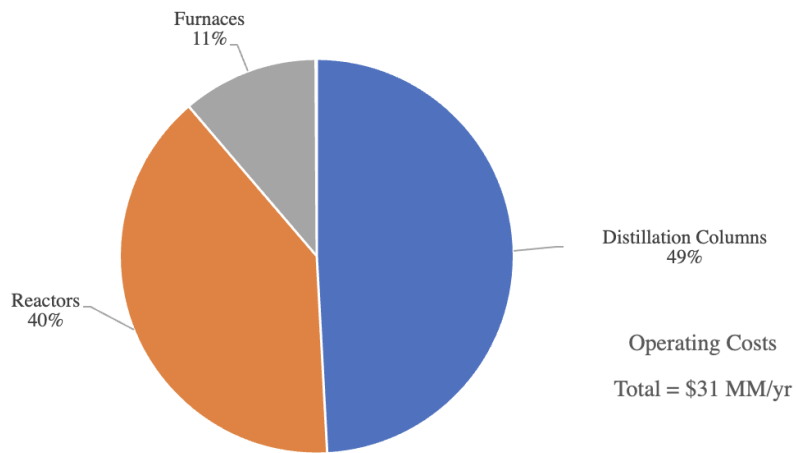
(b)

Figure 5. (a) Process equipment contributions towards the total ISBL. (b) Process equipment contributions towards the annual operating cost.

Figure 5 shows that the reactors and distillation columns account for the majority of the process equipment installed costs. There are 4 reactors and 6 distillation columns in the design. The electrolyzer is the most expensive reactor compared with the other three PFRs, having an installed cost of $ 26MM (see App. H). The distillation columns account for about 50% of the process annual operating cost; reactors also take up 40% of the total operating cost, in which the electrolyzer consumes the most electricity, having an operating cost of $6 MM/yr.

3.3 Sensitivity Analysis

Considering the price fluctuation of raw materials, carbon tax, catalysts and so on, a sensitivity analysis is carried on to observe the effects of price or cost changing on the design's profitability. This analysis is based on $\pm 15\%$ price fluctuations on the parameters listed in Figure 6. Price changing on propylene will bring the greatest NPV variations; a $\pm 15\%$ price fluctuation results in a NPV variation around 330%. The fluctuation on installed cost and operating cost also need to be noticed; a $\pm 15\%$ cost fluctuation results in a NPV variation around 100%.
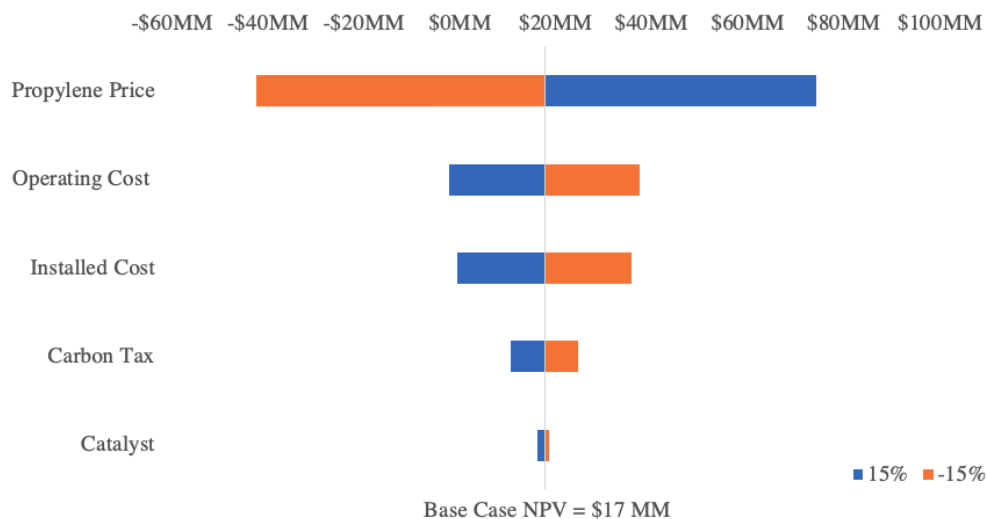
Figure 6. Tornado plot for the sensitivity of base case NPV in response to $\pm 15\%$ fluctuations in the listed properties.

This project design does not consider the recent volatility of oil prices and the inflation [2]. As this process is heavily dependent on the oil market, both for product price and feed price, large fluctuations in the price of propylene and propane may be seen. Also, the consumer price index in the United States was reported as 8.5% in the previous year [3]. Such high inflation increases the uncertainty of this sensitivity analysis.

4 Safety Considerations

The most hazardous events in the industrial chemical are corrosion and chemical fires, and these are greatest hazards for this plant chemistry as well. The existence of bromine, hydrobromic acid and hydrogen can cause significant corrosion on the process equipment, which may lead to leaks and damage [4,5,6]. Monel and stainless steel are desired materials to resist hydrobromic acid corrosion and hydrogen embrittlement respectively [7,8]. However, these materials may no longer prevent corrosion or hydrogen embrittlement in this plant because of the mix of either two of the chemicals [9,10]. Because of this, non conventional alternatives may need to be considered, such as Tantalum [11,12]. Nonetheless, the Tantalum use with halogens requires more research and development under temperatures higher than 100 °C. In addition, Tantalum is 20 times more expensive than Titanium [13], which would significantly increase the plant cost burden. As a result, a more detailed secondary analysis of material applicability is needed. The risks and costs associated with building materials should also be considered to determine a final material selection.

A considerable risk in this design lies in potential chemical fires, given that this process operates at high temperatures (above 300 °C) and pressures (above 10 bar). Considering the low auto ignition temperature of some chemicals in this design (see App. A), there is a significant risk of explosions and fire. Frequent maintenance and inspection of pumping networks are necessary to prevent any grinding or spark production within pump internals.

Some chemicals involved in this process have an NFPA (National Fire Protection Association) physical hazard rating of zero, such as hydrogen [14]. However, bromine poses a risk as an acute inhalation toxin, and has irritation of humans' mucous membranes in response to prolonged exposure. As a result, the toxic chemicals should be handled safely with precautions.

5 Conclusion & Final Recommendations

The techno-economic analysis performed in this report suggests that the project will make money, but whether the project is worth operating is still debatable. The project has a large TCI of $169 MM and an operating cost of $31 MM/yr. With a revenue around $ 65MM/yr, it will take several years to start making profits. Considering the recent volatility in the oil markets and inflation, this economic analysis is limited in scope. A more detailed analysis is needed.

The sensitivity analysis confirms that the profitability of this design depends most heavily on propylene selling price, so it is highly recommended that the management team negotiate a higher selling price for propylene to make more profits, or invest in this project with caution when propylene price falling down.

The distillation system is the largest component of total operating cost for the process, especially the reboilers consume large amounts of energy. The process development team may redesign the distillation system with the consideration of adjusting column pressure and preheating the feed into the distillation column to reduce the column operating cost.

The electrochemical reactor is the largest capital cost for the process. Most of the other equipment were also priced at a premium with titanium used as the base material to minimize the corrosion on the equipments by bromine, hydrogen and hydrobromic acid. As mentioned in safety and hazards, due to the unique challenges bromine, hydrobromic acid and hydrogen pose, further investigation into a cost-effective materials for this process must be conducted. If materials more expensive than Titanium is used, the economic calculations conducted in this report must be reevaluated.

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Appendix

A. Component Properties

Table A.1 . The physical properties for all species in the bromination process.

Species	Molar Mass (g/mol)	Heat of Combustion ΔH° (kJ/mol)	Auto Ignition Temperature (℃)	Boiling Temperature (℃)
Hydrogen (H_2)	2.016	-286	585	-253
Propane (C_3H_8)	44.097	-2220	450	-42
Bromine (Br_2)	159.8	-	N/A	58.8
n-Bromopropane (C_3H_7Br)	122.99	-2058	490	71
Hydrogen Bromide (HBr)	80.91	-	n/a	-66.8
Dibromopropane (C_3H_6Br2)	201.89	-	380	167
Propylene (C_3H_6)	42.08	-2058	458	-47.6

B. Chemical Reaction Kinetics and Operating Conditions of the Bromination of Propane Process

Propylene production reactions through bromination of propane are shown below [15]:

Sub-plant 1:

$$C_3H_8 + Br_2 \rightarrow C_3H_7Br + HBr \qquad \text{(R1)}$$

$$C_3H_7Br + Br_2 \rightarrow C_3H_6Br_2 + HBr \qquad \text{(R2)} \qquad \Delta H_2 = +21\,kJ$$

Sub-plant 1':

$$C_3H_6Br_2 + H_2 \rightarrow C_3H_7Br + HBr \qquad \text{(R3)} \qquad \Delta H_3 = -94\,kJ$$

Sub-plant 2:

$$C_3H_7Br \rightleftharpoons C_3H_6 + HBr \qquad \text{(R4)} \qquad \Delta H_4 = +113\,kJ$$

Sub-plant 3:

$$2HBr \rightarrow H_2 + Br_2 \qquad \text{(R5)} \qquad \Delta H_5 = +73\,kJ$$
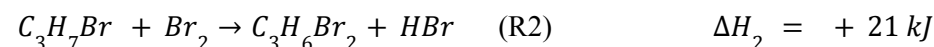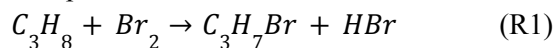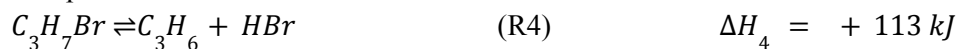
Sub-plant 1 reaction kinetics (99.5% conversion):

The first and second reaction (R1&R2) in sub-plant 1 follows the reaction rate expression below:

$$r_1 = k_1 [C_3 H_8] [Br_2] \text{ (1)}$$

$$r_2 = k_2 [C_3 H_7 Br] [Br_2] \text{ (2)}$$

Where

$$k_1 = 9.95 \times 10^{11} exp(- 112000/RT) \text{ (3)}$$

$$k_2 = 1.49 \times 10^{15} exp(- 155000/RT) \text{ (4)}$$

Where T is the temperature in Kelvin, $[C_3 H_8]$, $[C_3 H_7 Br]$, and $[Br_2]$ are the concentration of Propane, n-Bromopropane and Bromine. The activation energy is in J/gmol, R = 8.314J/(gmol K), and the concentrations of reacting species are in the units gmol/L. The units of k_1 and k_2 are L/(gmol h), thus the units of r_1 and r_2 are gmol/(L h).

The third reaction (R3) follows the reaction rate expression below:

$$r_3 = k_3 \left(\frac{[C_3 H_6 Br_2][H_2]}{1+(\frac{[H_2]}{K_{ad}})^3} \right) \text{ (5)}$$

Where

$$k_3 = 8.21 \times 10^7 exp(- 70000/RT) \text{ (6)}$$

And the hydrogen adsorption equilibrium constant, $K_{ad} = 0.6 \, gmol/L$.

Sub-plant 2 reaction kinetics:

The fourth reaction (R4) follows the reaction rate expression below:

$$r_4 = k_{4,f} [C_3 H_7 Br] - k_{4,r} [C_6 H_6][HBr] \text{ (7)}$$

Where

$$k_{4,f} = 2 \times 10^{14} exp(- 160000/RT) \text{ (8)}$$

$$k_{4,f} = 2 \times 10^{11} exp(- 160000/RT) \text{ (9)}$$

Operating Conditions:

The first two reactions in Sub-Plant 1 occur simultaneously in the same reactor within the temperature range 300-450 ℃ and a pressure of around 30 bar. The third catalytic reaction in Sub-Plant 1 takes place at a temperature of around 350 ℃ and a pressure of around 30 bar. The propylene production reaction in Sub-Plant 2 operates at a temperature of around 400 ℃ and a pressure of around 20 bar. The electrochemical cell operates at 25-75 ℃ and 10 bar pressure.

Catalyst Use:

According to the kinetic data propvided by Corporate R&D Department, hydrogenation catalyst in Sub-Plant 2 is a conventional extruded alumina supported palladium catalyst containing 5 wt% palladium sold by Haldor Topso Inc. The dehydrobromination catalyst is extruded silica sold by Johnson Matthey.

Table B.1. Price and parameters of the catalysts in the bromination process.

Catalyst	Price ($/kg)	Diameter (mm)	Length (mm)	Surface Area $(m^2/gram)$	Particle Density (kg/liter)	Void Fraction (%)
Hydrogenation	140	10	20	100	0.88	50
Dehydrobromination	10	15	25	100	0.5	50

C. Level 2 Analysis

Level 2 Flow Diagram
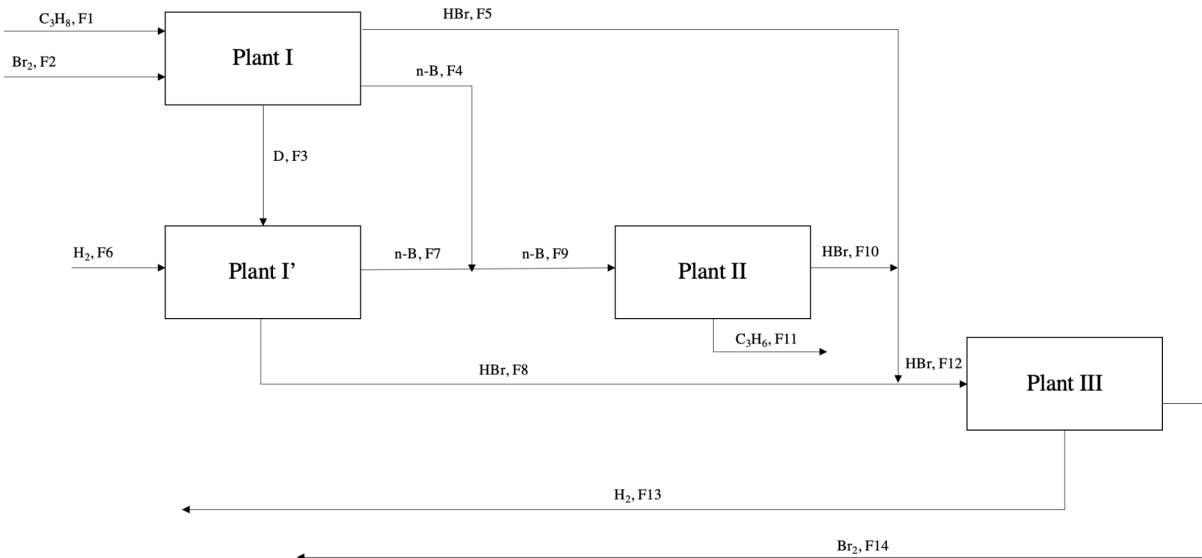
Figure C.1. Flow diagram of the level-2 bromination process. F1, F2 and F6 are fresh feeds of propane, bromine and hydrogen to the plants. F3 is dibromopropane steam. F12 is the combination of F5, F8 and F10; all of these are HBr streams. F9 is the combination f F4 and F7; all of these are n-bromopropane streams. F11 is the propylene production stream. F13 and F14 are hydorgne and bromine strams leaving the plants.

Level 2 balances:
Sub-plant I (5 species, 2 reactions):
Choose F1, F3 as reference
$$F2 = F1 + F3 \text{--------}(1)$$
$$F4 = F1 - F3 \text{--------}(2)$$
$$F5 = F1 + F3 \text{--------}(3)$$
$$s = \frac{F4}{F2} \text{--------}(4)$$

Sub-plant I' (4 species, 1 reaction):
Choose F6 as reference
$F3 = F6$ --------(5)
$F7 = F6$ --------(6)
$F8 = F6$ --------(7)

Sub-plant II (3 species, 1 reaction):
Choose F11 as reference
$F9 = F11$ --------(8)
$F10 = F11$ --------(9)

Sub-plant III (3 species, 1 reaction):
Choose F12 as reference
$2F13 = F12$ --------(10)
$2F14 = F12$ --------(11)
Balances of flow combinations:
$F12 = F5 + F8 + F10$ --------(12)
$F9 = F4 + F7$ --------(13)

Degree of freedom: # of unknown - # of equations = 15 - 13 = 2.
The equations system can be solved by speciftying two unknowns. As F11 (the desired production rate of propylene) is known, the level 2 balances can be solved by specifying a value of *s* (selectivity).

D. Level 3 Analysis
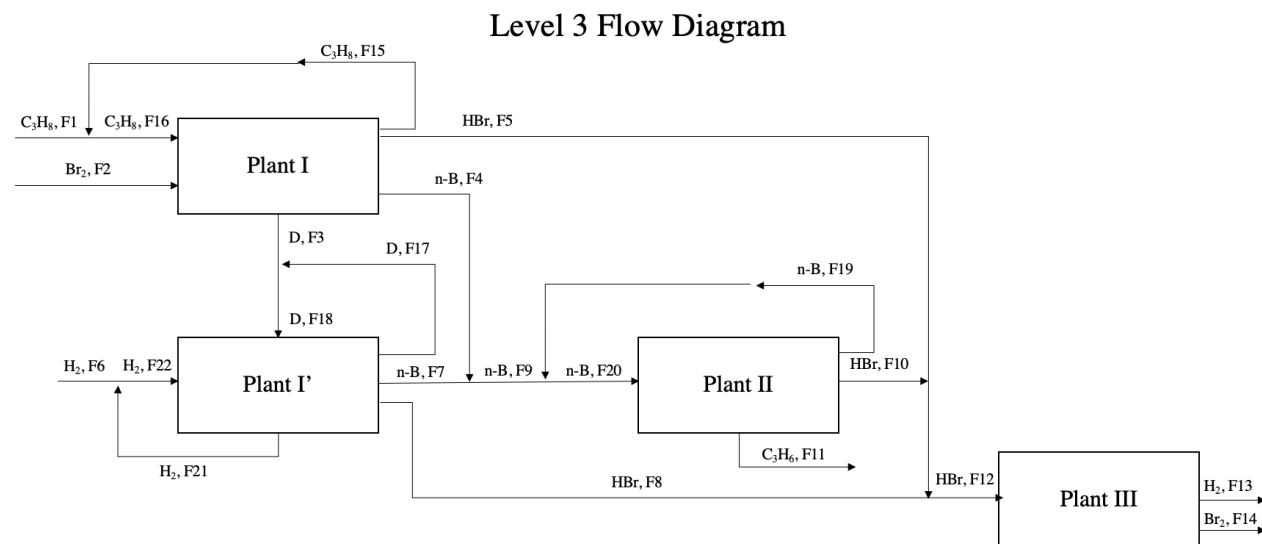
Figure D.1. Flow diagram of the level-3 bromination process. F15, F17, F19 and F21 are recycle streams of propane, dibromopropane, n-bromopropane and hydrogen based on level-2 flow diagram design.

Level 3 balances:

Sub-plant I (1 recycle)

Propane recycle:

$$MR1 = \frac{F16}{F2}$$

$$F15 = F16 - F1$$

Sub-plant I' (2 recycle)

Dibromopropane recycle:

$$x1' = \frac{F3}{F18}$$

$$F17 = F18 - F3$$

Hydrogen recycle:

$$MR1' = \frac{F22}{F18}$$

$$F21 = F22 - F6$$

Sub-plant II (1 recycle):

$$x2 = \frac{F9}{F20}$$

$$F19 = F20 - F9$$

E. Conceptual Design Optimization and PFD Stream Table

(a)   (b)

(c)

(d)

Figure E.1. (a) Volume of subplant 1 PFR reactor as a function of overall bromine conversion across the reactor at a fixed temperature but different propane to bromine molar ratios. Curves are generated at 350°C and 30 bar. (b) Selectivity of n-bromopropane in subplant 1 PFR reactor as a function of bromine conversion across the reactor at a fixed temperature but different propane to bromine molar ratios. Curves are generated at 350°C and 30 bar. (c) Volume of subplant 1 PFR reactor as a function of overall bromine conversion across the reactor at a fixed propane to bromine molar ratio of 3 but different temperature. Curves are generated at reactor pressure 30 bar. (d) selectivity of n-bromopropane in subplant 1 PFR reactor as a function of overall bromine conversion across the reactor at a fixed propane to bromine molar ratio of 3 but different temperature. Curves are generated at 30 bar.

Table E.1. Conceptual design optimization calculations at 12 cases

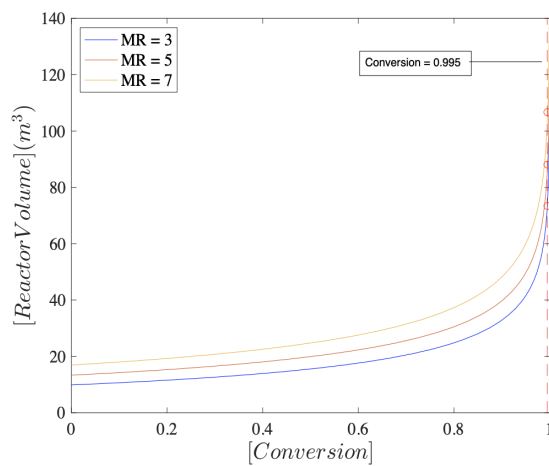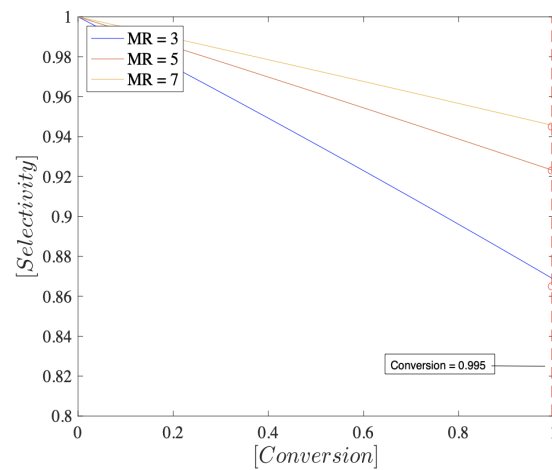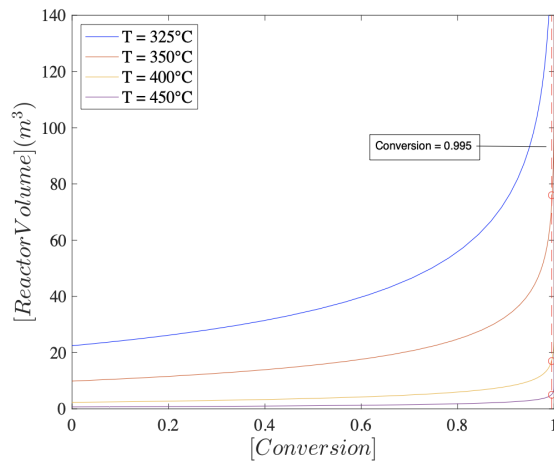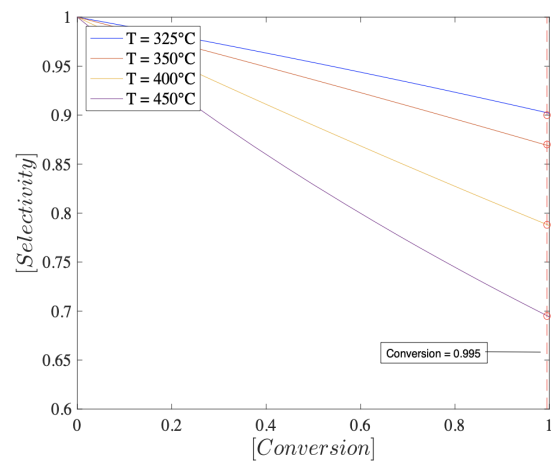| Molar Ratio	Temperature (°C)	selectivity	Reactor volume	reactor 1 Diameter(ft)	duty e104 *10^6 btu/h	duty e105	duty e106	duty e100	CapX reactor 1	heater e104	e105	e106	cooler e100	distillation T-105	total CapX	NPV
MR=3	325	0.9	175	15.48666984	11.65	10.63	31.14	19.44	1585267	537051	608205	1238681	1015987	2283000	28969944	180528029.2
	350	0.87	73	10.00231311	13.36	11.07	33.79	22.58	994751	603357	629538	1327727	1153883	2309500	28694008	181233164.2
	400	0.78	18	4.966783937	14.83	11.96	39.3	30.26	471654	659339	672308	1509637	1479909	2397000	28777598	181019553.2
	450	0.69	5	2.617724981	15.29	12.83	45.08	39	238295	676683	713656	1696387	1836122	2490200	29145895	180078400.3
MR=5	325	0.94	203	16.67965388	11.65	10.63	51.86	30.3	1715768	537051	608205	1910937	1481572	2990400	30238285	177286882.4
	350	0.92	88	10.98197249	13.36	11.07	56.28	35.38	1098936	603357	629538	2048518	1690210	3012100	30055311	177754459.1
	400	0.87	20	5.235449962	14.83	11.96	65.46	46.44	498898	659339	672308	2329262	2129879	3067900	30274438	177194496.9
	450	0.81	6	2.867574043	15.29	12.83	75.08	58.72	262614	676683	713656	2617185	2599948	3138000	30854838	175711330.3
MR=7	325	0.96	242	18.2115411	11.65	10.63	72.66	41.08	1884242	537051	608205	2545305	1919033	3587500	31478588	174117384.8
	350	0.94	112	12.38933587	13.36	11.07	78.85	47.98	1249673	603357	629538	2728476	2189766	3612400	31385562	174355105.2
	400	0.9	26	5.969331386	14.83	11.96	91.7	62.72	573778	659339	672308	3102078	2749740	3663500	31741995	173444270.4
	450	0.85	8	3.311189291	15.29	12.83	105.2	79.09	306133	676683	713656	3485353	3348882	3730000	32515460	171467740.5

Table E.2. PFD stream flow parameters (next page continued).

Stream	Flow Rate (kg/hr)	Flow Rate $\times 10^5$(MT/yr)	Energy Flow (MW)	T (°C)	P (bar)
FP1	11986	1.1	5.4	25	1
FP2	11986	1.1	5.4	25	30
FP3	11986	1.1	9.1	350	30
FB1	46347	4.1	0.01	25	1
FB2	46347	4.1	0.01	25	30
FB3	46347	4.1	3.3	350	30
FH1	23	2×10^{-3}	2×10^{-4}	25	30
F1	109360	9.6	23	350	30
F2	2740	0.24	0.08	232	30
F3	2740	0.24	0.24	350	30
F4	39954	3.5	2	164	20
F5	39954	3.5	7	400	20
F6	46347	4.1	5.8	18	20
F7	46347	4.1	8.1	75	20
P1	109361	9.6	36.5	350	30
P2	109361	9.6	26.8	150	30
P3	74315	6.5	37.6	67	30
P4	35045	3.1	6.7	230	30
P5	23174	2	4.2	35	30
P6	32078	2.8	6.4	229	30
P7	2740	0.24	0.5	350	30
P8	2740	0.24	0.3	150	30
P9	1142	0.1	0.2	36	30
P10	1598	0.14	0.3	228	30
P11	39954	3.5	3.4	400	20
P12	39954	3.5	0.6	200	20

Stream	Flow Rate (kg/hr)	Flow Rate $\times 10^5$ (MT/yr)	Energy Flow (MW)	T (°C)	P (bar)
P13	22032	1.9	3.9	14	20
P14	17922	1.6	0.25	51	20
P15	11416	1	0.55	47	20
P16	571	0.05	-	75	20
P17	45776	4	-	75	20
RP1	51142	4.5	21	68	30
RP2	51142	4.5	33.4	350	30
RD	2740	0.2	0.24	316	30
RN	6507	0.6	0.32	58	20

F. HYSYS Simulation of Optimized Process Design

The overall design of the plant is only as good as the model used to inform it. HYSYS simulation enables more accurate modeling of the process, resulting in a more accurate evaluation of plant economics. A detailed PFD for the HYSYS simulation can be found in Fig. on page . Even though the model used to produce the conceptual design is not as accurate as HYSYS simulations, it elucidates critical insights needed to motivate and expedite the simulation process.
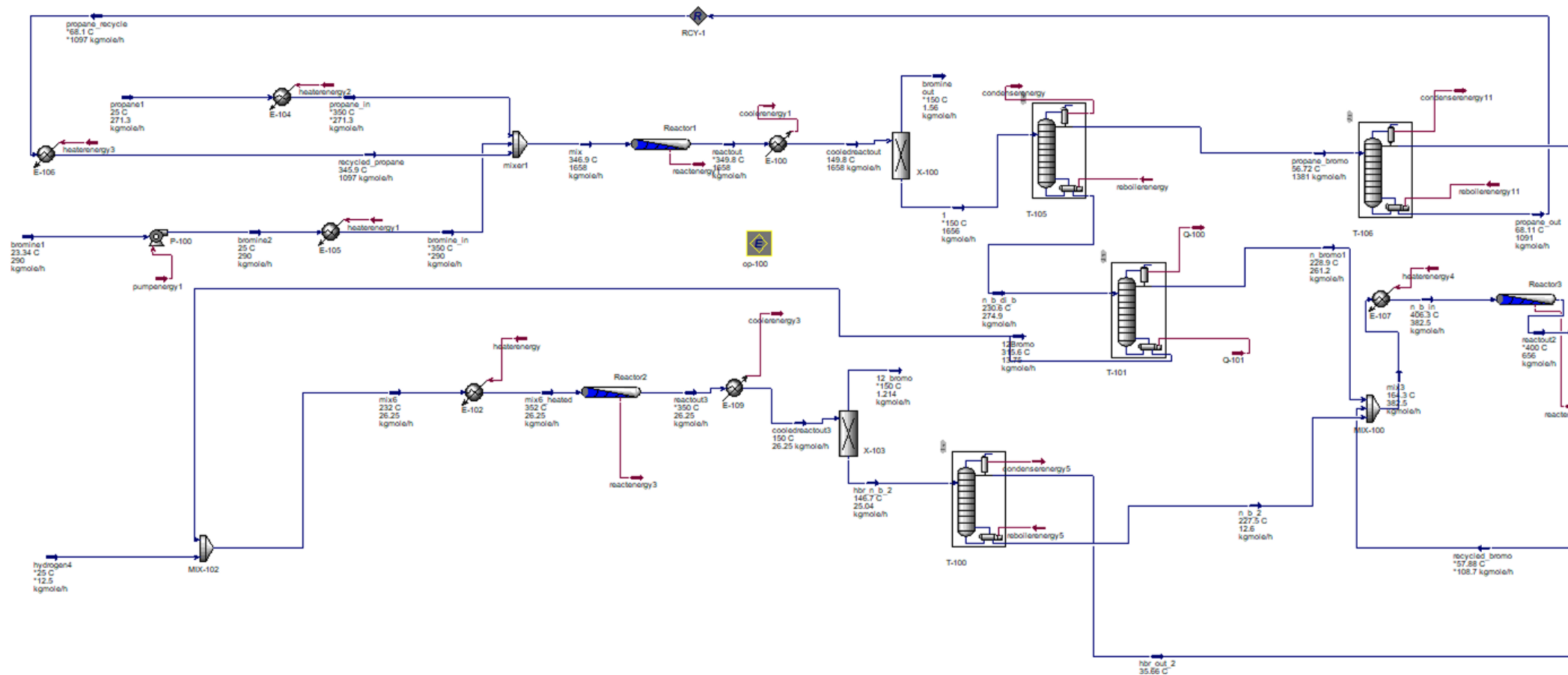
Figure F.1. HYSYS process flow diagram with labeled stream temperatures and flowrates for propylene production by bromination of propane plant.
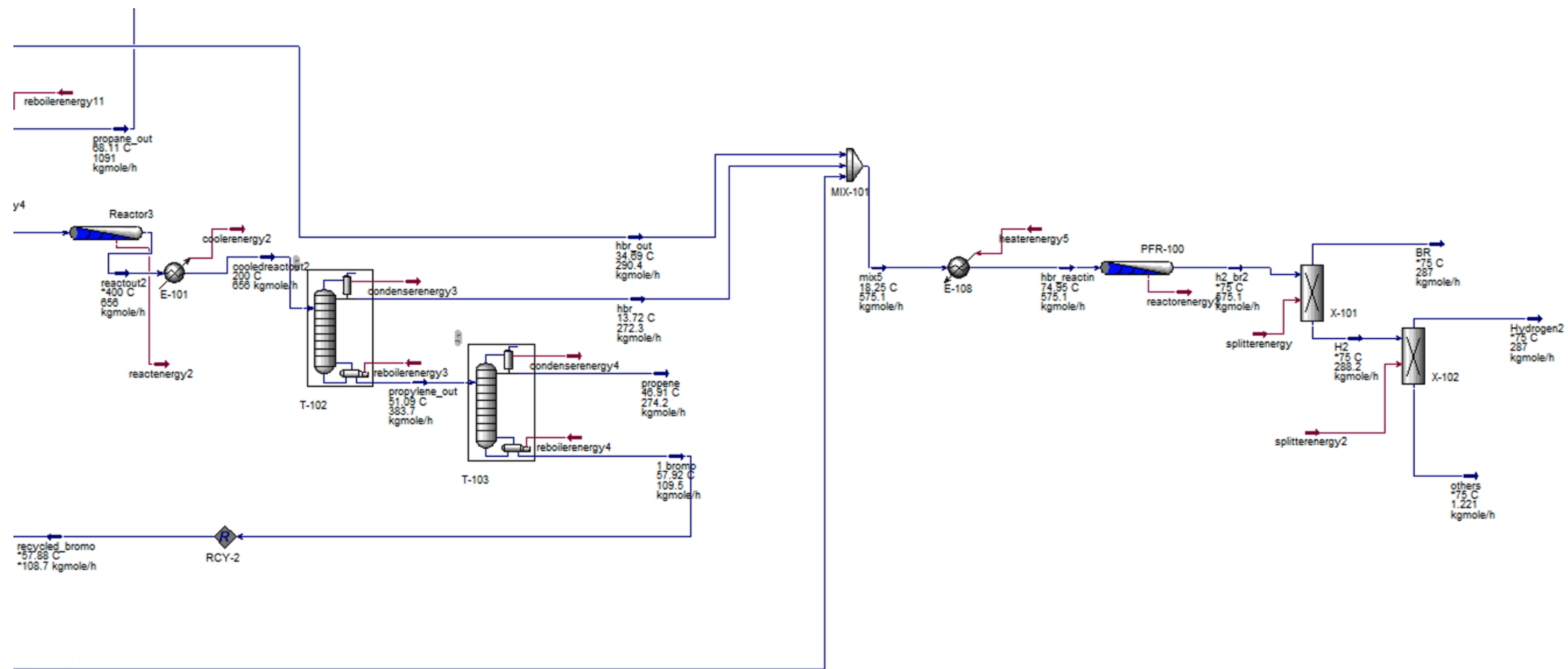
Figure F.2. HYSYS process flow diagram with labeled stream temperatures and flowrates for propylene production by bromination of propane plant (continued).

G. Heating System

G.1 Standard U Values

Table G.1. Typical properties for heating unit types and fluid types (Continued on next page). Source: Dimian et all 2008 p 321 [16].

Heating Unit Type	Hot Fluid	Cold Fluid	U $[\frac{W}{m^2°C}]$
Shell and Tube Heat Exchangers	Water	Water	800 - 1500
	Organic solvents	Organic solvents	100 - 300
	Light oils	Light oils	100 - 400
	Heavy oils	Heavy oils	50 - 300
	Reduced crude	Flashed crude	35 - 150
Heaters	Steam	Water	1500 - 4000
	Steam	Organic solvents	500 - 1000
	Steam	Light oils	300 - 900
	Steam	Heavy oils	60 - 450
	Steam	Gases	30 - 300
	Heat Transfer (hot) Oil	Heavy oils	50 - 300

Hot Fluid	Cold Fluid	U [$\frac{W}{m^2 \circ C}$]
Flue gases	Steam	30 - 100
Flue gases	Hydrocarbon vapours	30 -100

G.2 Pinch Analysis and Final Heat Table

Table G.2. HYSYS stream, reboiler, and condenser thermodynamic table.

Hot Stream	T1 (°C)	T2 (°C)	dT (°C)	dH (kW)	CpF (kJ/K)
H-104	25	350	325	3694	11
E-106	72	350	278	13550	49
E-105	25	350	325	3246	10
E-102	232	350	118	138.9	1
E-107	374	406	32	4838	151
E-108	18	75	57	2334	41
Column Reboiler					
T-105	230	236	6	4137	-
T-101	315	315	0.7	3448	-
T-106	77	77	0.3	9565	-
T-100	229	229	0.1	253.1	-
T-102	49	51	2.5	18150	-
T-103	50	58	8	3694	-
Cool Stream					
E-100	350	150	-200	-10450	52
E-109	350	26	-324	-185	1
E-101	400	200	-200	-2707	14

Column Condenser					
T-105	64	60	-4	-12090	-
T-101	229	227	-2	-3407	-
T-106	34	34	-0.02	-9251	-
T-100	36	36	-0.8	-267.9	-
T-102	17	14	-3	-22350	-
T-103	48	47	-1.3	-3692	-

From Figure G.1, the total trim area for all the non-distillation heat processes was found to be 13 MW. For this design process, however, some of the reboiler and codesers were also integrated to conserve more power. The final trim area was increased to 60 MW.
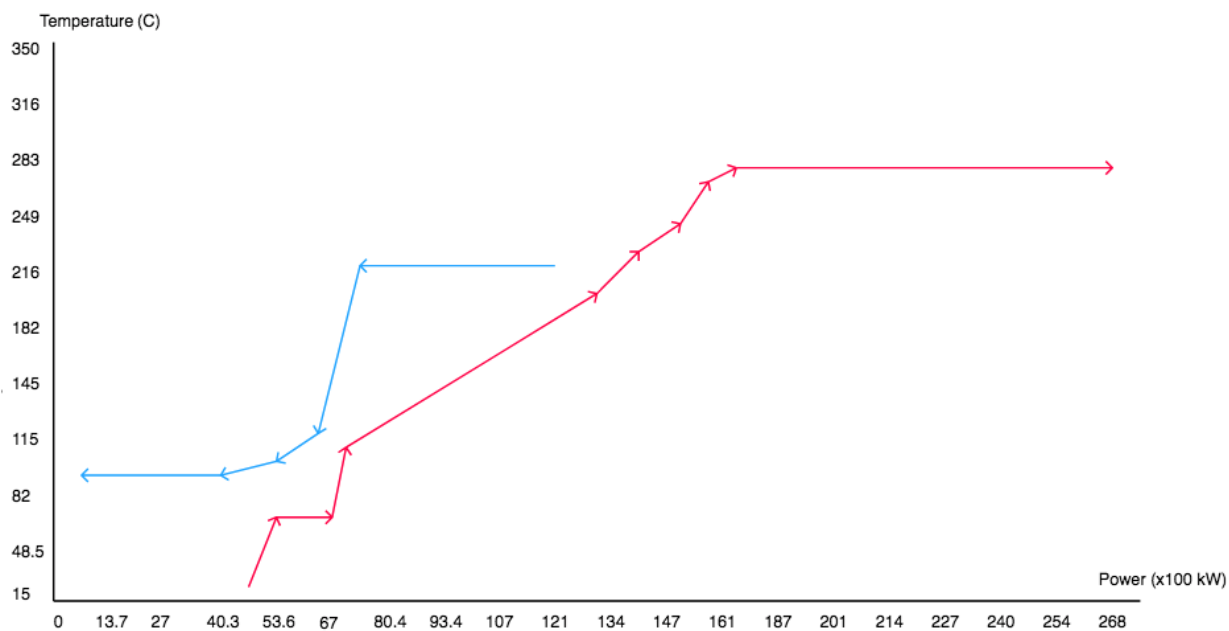

Figure G.1. Pinch Analysis of the thermodynamic system. The red line represents the heaters/reboilers and the blue line represents the coolers/condensers.

Table G.3. Bromination of propane conceptual design heat table.
*Heat X total as an group

HeatX	dH	dT	A (m^2)	A (ft^2)	Price	Water Cos/ Heat Transfer Fluid Cost	Total Cost
1	5,000	120	278	2,990	$2,645,886	N/A	N/A
2	5,450	80	454	4,889	$3,642,149	N/A	N/A
3	1,354	100	90	971	$1,273,962	N/A	N/A
4	1,354	100	90	971	$1,273,962	N/A	N/A
5*	12,090	15	5,373	57,838	$18,147,893	N/A	N/A
6	3,407	120	189	2,037	$2,061,971	N/A	N/A
7	2,334	15	1,037	11,166	$6,230,382	N/A	N/A
8	3,246	25	866	9,317	$5,538,906	N/A	N/A
Total Trim							
H-1	$393	N/A	N/A	N/A	$38,339	$54	$152,091
H-2	$3,624	N/A	N/A	N/A	$253,348	N/A	$1,402,488
H-3	$139	N/A	N/A	N/A	$15,838	N/A	$53,754
H-4	$4,838	N/A	N/A	N/A	$323,872		$1,872,306
Reboiler							
T-105	5,378	40	179	1,930	$1,365,070	$890,397	$2,971,683
T-101	3,448	40	115	1,237	$83,700	$570,861	$1,905,237
T-106	6,158	40	205	2,209	$1,490,690	$1,019,536	$3,402,682
T-100	$253	40	8	91	$187,189	$41,887	$139,798
T-102	6,060	40	202	2,174	$1,475,226	$1,003,311	$3,348,531
T-103	3,694	40	123	1,325	$87,535	$611,589	$2,041,167
Condenser							
T-106	-446	-20	30	320	$453,581	$33,617	$33,617
T-100	-268	-20	18	192	$24,961	$20,201	$20,201
T-102	-22,350	-10	2,980	32,076	$9,063,319	$3,508,950	$3,508,950
T-103	-1,358	-20	91	974	$935,346	$102,359	$102,359

Cooler					
C-1	34		$2,895	N/A	$12,974
Total			$57 MM	$7.8 MM	$21MM

H. Economic Calculations

Table H.1. PFD equipment parameters.
*For pricing purposes only not the the actual material (more details in Section 4 Safety and Hazards)

Equipment	Materials	Duty (MW)	Size	Installed Cost (MM$)
PFR 1	Solid Titanium*	3.8	$100\ m^3$	0.38
PFR 2	Solid Titanium*	0.2	$80\ m^3$	0.3
PFR 3	Solid Titanium*	5.2	$120\ m^3$	0.46
Electrochemical	N/A	2.6	N/A	26
Dist. Column 1	Solid Titanium*	37	$57\ m^3$	0.36
Dist. Column 2	Solid Titanium*	38	$72\ m^3$	0.56
Dist. Column 3	Carbon Steel	6.6	$54\ m^3$	0.28
Dist. Column 4	Solid Titanium*	0.5	$27\ m^3$	0.12
Dist. Column 5	Solid Titanium*	0.6	$74\ m^3$	0.56
Dist. Column 6	Carbon Steel	0.24	$52\ m^3$	0.28
Condenser 1	Solid Titanium*	1.2	$5373\ m^2$	7.2
Condenser 2	Solid Titanium*	0.4	$143\ m^2$	1
Condenser 3	Solid Titanium*	1.2	$143\ m^2$	7.24
Condenser 4	Solid Titanium*	0.3	$18\ m^2$	0.008
Condenser 5	Solid Titanium*	0.4	$880\ m^2$	2.4
Condenser 6	Solid Titanium*	0.4	$209\ m^2$	1
Reboiler 1	Solid Titanium*	5.3	$179\ m^2$	0.56
Reboiler 2	Solid Titanium*	6	$1042\ m^2$	3

Reboiler 3	Solid Titanium*	3.4	$114\ m^2$	0.032
Reboiler 4	Solid Titanium*	0.25	$8.4\ m^2$	0.08
Reboiler 5	Solid Titanium*	6	$209\ m^2$	1.4
Reboiler 6	Solid Titanium*	6.1	$205\ m^2$	0.6
Heat Exchangers 1	Solid Titanium*	10.1	$942\ m^2$	3.52
Heat Exchanger 2	Solid Titanium*	2.3	$1037\ m^2$	2.48
Heat Exchangers 3	Solid Titanium*	3.2	$866\ m^2$	2.2
Furnace 1	Solid Titanium*	3.6	-	0.1
Furnace 2	Solid Titanium*	0.1	-	0.008
Furnace 3	Solid Titanium*	0.3	-	0.016
Furnace 4	Solid Titanium*	4.8	-	0.13
Cooler 1	Solid Titanium*	3.4×10^{-5}	-	8×10^{-4}
Pump 1	Carbon Steel	1.7×10^{-5}	-	0.024
Pump 2	Carbon Steel	1.6×10^{-5}	-	0.024
Total ISBL				**$62 MM**

End of Year	Fixed Captial Investment	Working Capital	Start-up Capital	Salvage	Depreciation (d)	OpX/yr	Revenue (EP)	Profit After Tax (R-OpX-d)*(1-t)+d	Cash Flow (non-discout)	Cumulative Cash Flow (non-discount)		Cash Flow (discounted)	Cumulative Cash Flow (discounted)	IRR Calculation
		Discount Rate =	10%					Tax Rate =	27%					
0	0								0	0		0	0	0
1	-70680000								-70680000	-70680000		-64254545	-64254545.45	-63082790.45
2	-70680000	-1.4E+07	-14136000						-98952000	-169632000		-81778512	-146033057.9	-78823059.31
3					14842800	3.10E+07	6.00E+07	2.52E+07	25177556	-144454444		18916270.5	-127116787.4	17900148.59
4					14842800	3.10E+07	6.50E+07	2.88E+07	28827556	-115626888		19689608.6	-107427178.7	18292170.68
5					14842800	3.10E+07	6.50E+07	2.88E+07	28827556	-86799332		17899644.2	-89527534.53	16325992.79
6					14842800	3.10E+07	6.00E+07	2.52E+07	25177556	-61621776		14212074	-75315460.55	12726228.06
7					14842800	3.10E+07	6.50E+07	2.88E+07	28827556	-32794220		14793094.4	-60522366.16	13004938.74
8					14842800	3.10E+07	6.50E+07	2.88E+07	28827556	-3966664		13448267.6	-47074098.53	11607071.66
9					14842800	3.10E+07	6.00E+07	2.52E+07	25177556	21210892		10677741.5	-36396356.99	9047795.315
10					14842800	3.10E+07	6.50E+07	2.88E+07	28827556	50038448		11114270.8	-25282086.23	9245946.5
11					14842800	3.10E+07	6.50E+07	2.88E+07	28827556	78866004		10103882.5	-15178203.71	8252123.736
12					14842800	3.10E+07	6.00E+07	2.52E+07	25177556	104043560		8022345.26	-7155858.457	6432589.428
13						3.10E+07	6.50E+07	2.48E+07	24820000	128863560		7189469.91	33611.44823	5659634.618
14						3.10E+07	6.50E+07	2.48E+07	24820000	153683560		6535881.73	6569493.18	5051295.199
15		14136000		7068000		3.10E+07	6.50E+07	2.48E+07	46024000	199707560		11017779.7	17587272.86	8359873.168
														-41.27968385

NPV	17587272.86
NPV%	0.691193205
IRR	12.04323634

on-site (installed cost)	6.20E+07
OpX	3.10E+07
FCI	1.41E+08
SU	14136000
WC	14136000
TCI	169632000
S	7068000

Figure H.1 NPV Cash Flow Analysis spreadsheet.

I. Conceptual Design MATLAB Code

I.1 Codes for Solving PFR ODEs, Selectivity vs. Conversion, and Reactor Volume vs. Conversion

```matlab
clear all
clc;
%% Subplant 2

T2=400+273.15;
P2total=20*10^5; %unit Pa

R=8314; %unit Pa*L/(mol K)
Ppy_const=(10^8/42.08)/(10^-3*8760);%unit in mol/h, result = 271281

y20 = [271281 0 0 271281];%initial condition on reactor inlet/outlet flowrate, unit mol/h

V2span=[0 200000]; %reactor volume
[V2,F2]=ode45(@(V2,F2) subplant2(V2,F2,R,T2,P2total),V2span,y20);

F2nB0 = 271281;  %assume a consatnt FnB0 (flowrate of n-Bromopropane at time 0)
F2nB=F2(:,1); % F matrix is the resulting of running ode.m, FnB correspnds to the first column of F
x_subplant2 = (F2nB0-F2nB)./(F2nB0);

Volume2 = V2(:,1).*10^(-3); % V matrix got from ode.m, unit in m3

sumFreal2 = Ppy_const./x_subplant2;
sumF2 = Ppy_const;
V2real = (Volume2.*sumFreal2)./sumF2;

figure(1)
plot(x_subplant2,V2real,'Color','b')
xlim([0 1]);
hold on
plot([0 0.88], [43 43], 'r','LineStyle','--')
plot([0.88 0.88], [0 43], 'r','LineStyle','--')
scatter(0.88, 43,'r')
a =gca; set(a,'Fontsize',15,'FontName','Times');%,'XTick',[0:0.1:0.8],'YTick',[-3:0.5:2]);
xl = xlabel('$[Conversion]$','interpreter','latex'); yl = ylabel('$[Volume] (m^3)$','interpreter','latex');
set(xl,'Fontsize',20,'FontName','Times');set(yl,'Fontsize',20,'FontName','Helvetica');
lgd = legend('Subplant2 Reactor','location','northwest');
lgd.FontSize = 15;
%%

%% Subplant1 reactor2

T12=350+273.15;
P12total=30*10^5; %unit Pa
MR12 = 3;
MR12_2 = 7;
MR12_3 = 9;

F12dB0 = 18859;  %F7
PnBconst12 = 18859;

%æ"¹
```

```
y120 = [F12dB0 F12dB0*MR12 0 0 F12dB0*(1+MR12)];%initial condition on reactor inlet/outlet flowrate, unit mol/h
y120_2 = [F12dB0 F12dB0*MR12_2 0 0 F12dB0*(1+MR12_2)];
y120_3 = [F12dB0 F12dB0*MR12_3 0 0 F12dB0*(1+MR12_3)];
V12span=[0 200000]; %reactor volume

[V12,F12]=ode45(@(V12,F12) subplant1_r2(V12,F12,R,T12,P12total),V12span,y120);
[V12_2,F12_2]=ode45(@(V12,F12) subplant1_r2(V12,F12,R,T12,P12total),V12span,y120_2);
[V12_3,F12_3]=ode45(@(V12,F12) subplant1_r2(V12,F12,R,T12,P12total),V12span,y120_3);


F12dB=F12(:,1); % F matrix is the resulting of running ode.m, FnB correspnds to the first column of F
x_subplant12 = (F12dB0-F12dB)./(F12dB0);
F12dB_2=F12_2(:,1);
x_subplant12_2 = (F12dB0-F12dB_2)./(F12dB0);
F12dB_3=F12_3(:,1);
x_subplant12_3 = (F12dB0-F12dB_3)./(F12dB0);

Volume12 = V12(:,1).*10^(-3); % V matrix got from ode.m, unit in m3
Volume12_2 = V12_2(:,1).*10^(-3);
Volume12_3 = V12_3(:,1).*10^(-3);


sumFreal12 = PnBconst12*(1+MR12)./x_subplant12;
sumF12 = PnBconst12*(1+MR12);
V12real = (Volume12.*sumFreal12)./sumF12;
sumFreal12_2 = PnBconst12*(1+MR12_2)./x_subplant12_2;
sumF12_2 = PnBconst12*(1+MR12_2);
V12real_2 = (Volume12_2.*sumFreal12_2)./sumF12_2;
sumFreal12_3 = PnBconst12*(1+MR12_3)./x_subplant12_3;
sumF12_3 = PnBconst12*(1+MR12_3);
V12real_3 = (Volume12_3.*sumFreal12_3)./sumF12_3;

figure(2)
plot(x_subplant12,V12real,'Color','b')
ylim([0 60]);
hold on
plot(x_subplant12_2,V12real_2);
plot(x_subplant12_3,V12real_3);
plot([0.92 0.92], [0 60], 'r','LineStyle','--')
scatter (0.92,11,'r')
scatter (0.92,20,'r')
scatter (0.92,25.5,'r')
a =gca; set(a,'Fontsize',15,'FontName','Times');%,'XTick',[0:0.1:0.8],'YTick',[-3:0.5:2]);
xl = xlabel('$[Conversion]$','interpreter','latex'); yl = ylabel('$[Volume] (m^3)$','interpreter','latex');
set(xl,'Fontsize',20,'FontName','Times');set(yl,'Fontsize',20,'FontName','Helvetica');
lgd = legend('MR = 3','MR = 7','MR = 9','location','northwest');
lgd.FontSize = 15;



%% subplant1 reactor1

P11total=30*10^5; %unit Pa
MR11_1 = 3;
MR11_2 = 5;
MR11_3 = 7;

F11Br0 = 252420;  %F4
PnBconst11 = 252420; %assume we know product rate is a constant 136000

y110_1 = [MR11_1*F11Br0 F11Br0 0 0 0 F11Br0*(1+MR11_1)];%initial condition on reactor inlet/outlet flowrate, unit mol/h
V11span=[0 300000];

% T11 = 573:723;
T11=325+273.15;
```

```matlab
[V11_1,F11_1]=ode45(@(V11,F11) subplant1_r1(V11,F11,R,T11,P11total),V11span,y110_1);
T11=350+273.15;
[V11_2,F11_2]=ode45(@(V11,F11) subplant1_r1(V11,F11,R,T11,P11total),V11span,y110_1);
T11=400+273.15;
[V11_3,F11_3]=ode45(@(V11,F11) subplant1_r1(V11,F11,R,T11,P11total),V11span,y110_1);
T11=450+273.15;
[V11_4,F11_4]=ode45(@(V11,F11) subplant1_r1(V11,F11,R,T11,P11total),V11span,y110_1);

F11Br_1=F11_1(:,2); % F matrix is the resulting of running ode.m, FnB correspnds to the first column of F
x_subplant11_1 = (F11Br0-F11Br_1)./(F11Br0);
F11Br_2=F11_2(:,2);
x_subplant11_2 = (F11Br0-F11Br_2)./(F11Br0);
F11Br_3=F11_3(:,2);
x_subplant11_3 = (F11Br0-F11Br_3)./(F11Br0);
F11Br_4=F11_4(:,2);
x_subplant11_4 = (F11Br0-F11Br_4)./(F11Br0);

Volume11_1 = V11_1(:,1).*10^(-3); % V matrix got from ode.m, unit in m3
Volume11_2 = V11_2(:,1).*10^(-3);
Volume11_3 = V11_3(:,1).*10^(-3);
Volume11_4 = V11_4(:,1).*10^(-3);

PnB11_1=F11_1(:,3);
PnB11_2=F11_2(:,3);
PnB11_3=F11_3(:,3);
PnB11_4=F11_4(:,3);

s_subplant11_1 = PnB11_1./(F11Br0-F11Br_1);
s_subplant11_2 = PnB11_2./(F11Br0-F11Br_2);
s_subplant11_3 = PnB11_3./(F11Br0-F11Br_3);
s_subplant11_4 = PnB11_4./(F11Br0-F11Br_4);

figure (3)
plot(x_subplant11_1,s_subplant11_1,'Color','b');
xlim([0 1]);
ylim([0.6 1]);
hold on
plot(x_subplant11_2,s_subplant11_2);
plot(x_subplant11_3,s_subplant11_3);
plot(x_subplant11_4,s_subplant11_4);
plot([0.995 0.995], [0 1], 'r','LineStyle','--')
scatter (0.995,0.9,'r')
scatter (0.995,0.87,'r')
scatter (0.995,0.788,'r')
scatter (0.995,0.695,'r')
a =gca; set(a,'Fontsize',15,'FontName','Times');%,'XTick',[0:0.1:0.8],'YTick',[-3:0.5:2]);
xl = xlabel('$[Conversion]$','interpreter','latex'); yl = ylabel('$[Selectivity] $','interpreter','latex');
set(xl,'Fontsize',20,'FontName','Times');set(yl,'Fontsize',20,'FontName','Helvetica');
lgd = legend('T = 325°C','T = 350°C','T = 400°C','T = 450°C','location','northwest');
lgd.FontSize = 15;


sumFreal11_1 = PnBconst11*(1+MR11_1)./(x_subplant11_1.*s_subplant11_1);
sumF11_1 = PnBconst11*(1+MR11_1);
V11real_1 = (Volume11_1.*sumFreal11_1)./sumF11_1;
sumFreal11_2 = PnBconst11*(1+MR11_1)./(x_subplant11_2.*s_subplant11_2);
sumF11_2 = PnBconst11*(1+MR11_1);
V11real_2 = (Volume11_2.*sumFreal11_2)./sumF11_2;
sumFreal11_3 = PnBconst11*(1+MR11_1)./(x_subplant11_3.*s_subplant11_3);
sumF11_3 = PnBconst11*(1+MR11_1);
V11real_3 = (Volume11_3.*sumFreal11_3)./sumF11_3;
sumFreal11_4 = PnBconst11*(1+MR11_1)./(x_subplant11_4.*s_subplant11_4);
sumF11_4 = PnBconst11*(1+MR11_1);
V11real_4 = (Volume11_4.*sumFreal11_4)./sumF11_4;
```

```
figure(4)
plot(x_subplant11_1,V11real_1,'Color','b');
ylim([0 140]);
xlim([0 1]);
hold on
plot(x_subplant11_2,V11real_2);
plot(x_subplant11_3,V11real_3);
plot(x_subplant11_4,V11real_4);
plot([0.995 0.995], [0 140], 'r','LineStyle','--')
scatter (0.995,76,'r')
scatter (0.995,17,'r')
scatter (0.995,5,'r')
a =gca; set(a,'Fontsize',15,'FontName','Times');%,'XTick',[0:0.1:0.8],'YTick',[-3:0.5:2]);
xl = xlabel('$[Conversion]$','interpreter','latex'); yl = ylabel('$[Reactor Volume] (m^3)$','interpreter','latex');
set(xl,'Fontsize',20,'FontName','Times');set(yl,'Fontsize',20,'FontName','Helvetica');
lgd = legend('T = 325Â°C','T = 350Â°C','T = 400Â°C','T = 450Â°C','location','northwest');
lgd.FontSize = 15;
%%% varying MR of subplant1 reactor 1
y110_2 = [MR11_2*F11Br0 F11Br0 0 0 0 F11Br0*(1+MR11_2)];
y110_3 = [MR11_3*F11Br0 F11Br0 0 0 0 F11Br0*(1+MR11_3)];


% T11 = 573:723;
T11=350+273.15; %assume at constant T, see the effect of varyig MR on selectivity and volume
[V11_MR2,F11_MR2]=ode45(@(V11,F11) subplant1_r1(V11,F11,R,T11,P11total),V11span,y110_2);
[V11_MR3,F11_MR3]=ode45(@(V11,F11) subplant1_r1(V11,F11,R,T11,P11total),V11span,y110_3);



F11Br_MR2=F11_MR2(:,2);
x_subplant11_MR2 = (F11Br0-F11Br_MR2)./(F11Br0);
F11Br_MR3=F11_MR3(:,2);
x_subplant11_MR3 = (F11Br0-F11Br_MR3)./(F11Br0);

Volume11_MR2 = V11_MR2(:,1).*10^(-3);
Volume11_MR3 = V11_MR3(:,1).*10^(-3);

PnB11_MR2=F11_MR2(:,3);
PnB11_MR3=F11_MR3(:,3);


s_subplant11_MR2 = PnB11_MR2./(F11Br0-F11Br_MR2);
s_subplant11_MR3 = PnB11_MR3./(F11Br0-F11Br_MR3);


figure (5)
plot(x_subplant11_2,s_subplant11_2,'Color','b');
xlim([0 1]);
ylim([0.8 1]);
hold on
plot(x_subplant11_MR2,s_subplant11_MR2);
plot(x_subplant11_MR3,s_subplant11_MR3);
plot([0.995 0.995], [0 1], 'r','LineStyle','--')
scatter (0.995,0.865,'r')
scatter (0.995,0.923,'r')
scatter (0.995,0.945,'r')
a =gca; set(a,'Fontsize',15,'FontName','Times');%,'XTick',[0:0.1:0.8],'YTick',[-3:0.5:2]);
xl = xlabel('$[Conversion]$','interpreter','latex'); yl = ylabel('$[Selectivity] $','interpreter','latex');
set(xl,'Fontsize',20,'FontName','Times');set(yl,'Fontsize',20,'FontName','Helvetica');
lgd = legend('MR = 3','MR = 5','MR = 7','location','northwest');
lgd.FontSize = 15;


sumFreal11_MR2 = PnBconst11*(1+MR11_2)./(x_subplant11_MR2.*s_subplant11_MR2);
sumF11_MR2 = PnBconst11*(1+MR11_2);
V11real_MR2 = (Volume11_MR2.*sumFreal11_MR2)./sumF11_MR2;
sumFreal11_MR3 = PnBconst11*(1+MR11_3)./(x_subplant11_MR3.*s_subplant11_MR3);
sumF11_MR3 = PnBconst11*(1+MR11_3);
V11real_MR3 = (Volume11_MR3.*sumFreal11_MR3)./sumF11_MR3;
```

```matlab
figure(6)
plot(x_subplant11_2,V11real_2,'Color','b');

ylim([0 140]);
hold on
plot(x_subplant11_MR2,V11real_MR2);
plot(x_subplant11_MR3,V11real_MR3);
plot([0.995 0.995], [0 140], 'r','LineStyle','--')
scatter (0.995,73.4,'r')
scatter (0.995,88.1,'r')
scatter (0.995,106.7,'r')
a =gca; set(a,'Fontsize',15,'FontName','Times');%,'XTick',[0:0.1:0.8],'YTick',[-3:0.5:2]);
xl = xlabel('$[Conversion]$','interpreter','latex'); yl = ylabel('$[Reactor Volume] (m^3)$','interpreter','latex');
set(xl,'Fontsize',20,'FontName','Times');set(yl,'Fontsize',20,'FontName','Helvetica');
lgd = legend('MR = 3','MR = 5','MR = 7','location','northwest');
lgd.FontSize = 15;

%% Subplant1 Reactor1 ODE

function Y11 =subplant1_r1(V11,F11,R,T11,P11total) % V in m^3, F in mol/h

Y11 = zeros(6,1);

k1 = 9.95*10^11*exp(-112000/(8.314*T11));
k2 = 1.49*10^15*exp(-155000/(8.314*T11));

r1 = k1*(P11total^2*F11(1)*F11(2)/(F11(6)^2*R^2*T11^2)); %unit mol/(L*h)
r2 = k2*(P11total^2*F11(3)*F11(2)/(F11(6)^2*R^2*T11^2));

Y11(1) = -r1; %Propane
Y11(2) = -r1-r2; %Br
Y11(3) = r1-r2; %n-Bromopropane
Y11(4) = r1+r2; %HBr
Y11(5) = r2; %dibromopropane
Y11(6) = 0; %total
end

%% Subplant1 reactor2 ODE


function Y12 =subplant1_r2(V12,F12,R,T12,P12total) % V in m^3, F in mol/h

Y12 = zeros(5,1);

k3 = 8.21*10^7*exp(-70000/(8.314*T12));
r3 = k3*(P12total^2*F12(1)*F12(2)/(F12(5)^2*R^2*T12^2))/(1+(F12(2)*P12total/(F12(5)*R*T12*0.6))^3); %unit mol/(L*h)

Y12(1) = -r3; %dibromopropane
Y12(2) = -r3; %H2
Y12(3) = r3; %n-Bromopropane
Y12(4) = r3; %HBr
Y12(5) = 0; %total
end
```

```matlab
function Y2 =subplant2(V2,F2,R,T2,P2total) % V in m^3, F in mol/h

Y2 = zeros(4,1);

k4f = 2*10^14*exp(-160000/(8.314*T2));
k4r = 2*10^11*exp(-130000/(8.314*T2));

r4 = k4f*P2total*F2(1)/(F2(4)*R*T2)-k4r*P2total^2*F2(2)*F2(3)/(F2(4)^2*R^2*T2^2);%unit in mol/(L*h)

Y2(1)= -r4; %n-B
Y2(2) = r4; %propylene
Y2(3) = r4; %HBr
Y2(4) = r4; %total
end
```

I.2 Codes for Distillation System Design (Column T-105 as the example)

```matlab
%T-105

F = (F5+F4+F15+F3)*10^(-3);% kmol/hr
%T = 595.6+273.15; % in K
P = 3000; % in kPa
z1 = F5/(F5+F4+F15+F3); % 1 is hbr
z2 = F15/(F5+F4+F15+F3); % 2 is propane
z3 = F4/(F5+F4+F15+F3); % 3 is n-bromopropane
z4 = F3/(F5+F4+F15+F3); % 4 is 1,2 bromopropane
q = 1;


BDVLE=readmatrix('benzene_diphenyl.txt');
x1 = BDVLE(:,1);
y1 = BDVLE(:,2);
TDVLE=readmatrix('toluene_diphenyl.txt');
x2 = TDVLE(:,1);
y2 = TDVLE(:,2);

a1 = 13.59; %a_PD
a2 = 18.16; %a_HbrD
a3 = 2.046; %a_NbroD
a5 = 1.658; %a_HbrP

%calculate r min, table4.1
R_min = (a3*z1/(a1-a3)+a3*(z2+z3)/(a2-a3))/((z1+z2)*(1+z1*(z3+z4)))+z4*(z1/(a1-1)+z2/(a2-1))/((z1+z2)^2);

R = 1.5*R_min;
D = F*(z1+z2);
B = F*(z3+z4);
s = D/B*(R+q)-(1-q);
a_avg = (a1 * a2*a3)^(1/3); % take average of alpha    % calculate N min
Nmin = log((0.998*0.997)/((1-0.998)*(1-0.997)))/(log(a_avg));

%calculate N
syms N
eqn = (N-Nmin)/(N+1) == 0.75*(1-((R-R_min)/(R+1))^0.5688);
N = solve(eqn,N,'Real',true);
N = double (N);
N_real = 2*N; % the real number of stages N real

V_B = s*B; %kmol/h
V_T = (R+1)*D;
L_B = B*(1+s);
```

```
L_T = R*D;

%heat
Lamda_D = (17.15*z1/(z1+z2)+16.25*z2/(z1+z2))*10^3; % molar latent heat of distillate (benzene) in kJ/kmol
Lamda_B = (29.84*z3/(z3+z4)+41.78*z4/(z3+z4))*10^3; % molar latent heat of bottom (toluene and diphenyl) in kJ/kmol


% heat loads on the condenser and reboiler
Q_C = Lamda_D*V_T; % kJ/hr
Q_R = Lamda_B*V_B; % kJ/hr

% column diameter
p_hbr = 2603; % liquid toluene density in kg/m^3
p_hbr2 = 3.45; % gas toluene density in kg/m^3
p_propane = 493; % liquid benzene density in kg/m^3
p_propane2 = 2.01;% gas benzene density in kg/m^3
p_nbromo = 1354; % diphenyl density in kg/m^3
p_nbromo2 = 4.3;
p_dibromo =1971.2;
p_dibromo2 = 7;
p_h2 = 71;
p_h22 = 0.08375;
MW_Vtop = 80.91*z1/(z1+z2)+44.097*z2/(z1+z2); % vapor molecular weight(kg/kmol), mostly benzene
MW_Vbot = 122.99*z3/(z3+z4)+201.89*z4/(z3+z4); %molecular weight

p_vt = p_hbr2*z1/(z1+z2)+p_propane2*z2/(z1+z2);
p_lt = p_hbr*z1/(z1+z2)+p_propane*z2/(z1+z2);
p_vb = p_nbromo2*z3/(z3+z4)+p_dibromo2*z4/(z3+z4);
p_lb = p_nbromo*z3/(z3+z4)+p_dibromo*z4/(z3+z4);


ft = (L_T/V_T)*(p_vt/p_lt)^0.5; %flow parameter at top, D&M Eqn 6.7
fb = (L_B/V_B)*(p_vb/p_lt)^0.5; %flow parameter at bottom
ct = 439/(1+2.5*ft^1.2); %capaccity parameter at the top, choose tray spacing 24 in, c unit in m/h
cb = 439/(1+2.5*fb^1.2);
Ft_flood = 0.8*(p_lt)^0.5*ct; %at top, D&M eqn 6.10
Fb_flood = 0.8*(p_lb)^0.5*cb;

% column height
H_t = 0.6; % meters
H = 3*H_t +H_t*N_real %unit m
Hft = H*3.28

% reboiler and condenser heat exchange
MW_Vavg = (MW_Vtop+MW_Vbot)/2;
p_lavg = (p_lt+p_lb)/2;
p_vavg = (p_vt+p_vb)/2;
c_avg = (ct+cb)/2;
Vavg = (V_T+V_B)/2;
A_avg = (MW_Vavg*1.25*Vavg)/((p_vavg*p_lavg)^0.5*0.6*c_avg);
D_avg = 2*sqrt(A_avg/3.14); %unit m2
D_avgft = D_avg*3.28
```

I.3 Codes for Conceptual Equipment Installed Cost, Catalyst Cost and Economic Potential Calculations

```
clc;
clear all
% Marshall and Swift Index
MS = 1650;


%heater
```

```matlab
Q = 14;%btu/hr
fd_heat = 1.00;
fm_heat = 0.5; %SS
%fm_heat =0; %CS
fp_heat = 0;
fc_heat = fd_heat+fm_heat+fp_heat;
ISBL_heater = (MS/280)*(5.07*10^3)*Q^0.85*(1.23+fc_heat)


%furnance
Q = 36;
fd_fur = 1.00;
%fm_fur = 0.75; %SS
fm_fur =0.; %CS
fp_fur = 0;
fc_fur = fd_fur+fm_fur+fp_fur;
ISBL_furnace = (MS/280)*(5.52*10^3)*Q^0.85*(1.27+fc_fur)


%{
% compressors
% purchased cost
a1 = MS./280.*517.5*100.^0.82.*1.29;
% installed cost
b1 = MS./280.*517.5*100.^0.82.*(2.11+1.29);
% total cost
t1 = a1+b1;
%}


% reactor

D = 5.23;   %unit in ft
H1 = 32.8;   %unit in ft, 10m
MS =  1650;
%Fp1 = 1.2;  %from App.E table pp.574, 20bar
Fp1 = 1.4; % 30bar
Fm1 = 4.25; %choose titanium slad, because distillation column withstand high P
 %Fm1 = 1; % CS
Fc1 = Fm1*Fp1;
ISBL_reactor=(MS/280)*101.9*D^1.066*H1^0.82*(2.18+Fc1)



%ISBL for column shell
D = 16.0666;  %unit in ft
H1 = 68.4577;   %unit in ft
MS =  1650;
%Fp1 = 1.2;  %from App.E table pp.574, 20bar
Fp1 = 1.4; % 30bar
Fm1 = 4.25; %choose titanium slad, because distillation column withstand high P
 %Fm1 = 1; % CS
Fc1 = Fm1*Fp1;
ISBL_columnshell=(MS/280)*101.9*D^1.066*H1^0.82*(2.18+Fc1)



% ISBL for column trays
H2 = 24;             %tray stack height in ft
Fs2 = 1.0;             % from App.E pp.575
Ft2 = 0; %choose sieve
Fm2 = 8.9; % monel
%Fm2 = 0; %CS
Fc2 = Fs2+Ft2+Fm2;
ISBL_columntray = (MS/280)*4.7*D^1.55*H2*Fc2

%ISBL for reboiler
A_reboiler = 48; %unit in ft2
Fd3 =  1.35;  %from App.E pp.572
%Fp3 = 0.10; % 20bar
```

```
Fp3  = 0.3 % 30bar
%Fm3 = 1; %carbon shell
 Fm3  = 8.95; %ti
Fc3 = (Fd3+Fp3)*Fm3;
ISBL_reboiler = (MS/280)*101.3*A_reboiler^0.65*(2.29+Fc3)


%ISBL for condenser
A_condenser = 48;
Fd4 = 1.00;
%Fp4 = 0.10; %20bar
 Fp4 = 0.3; %30 bar
%Fm4 = 1; %carbon shell
 Fm4 = 8.95; %ti slad
Fc4 = (Fd4+Fp4)*Fm3;
ISBL_condenser = (MS/280)*101.3*A_condenser^0.65*(2.29+Fc4)


Tot = ISBL_columnshell+ISBL_columntray+ISBL_reboiler+ISBL_condenser
% Substance Price
C3H6 = 900; %propylene $/MT
C3H8 = 200; %propane $/MT
H2 = 1400; %hydrogen gas feed $/MT
Br2 = 3000; %Br2 feed $/MT
CO2 = 75; %CO2 charge $/MT
Fuel = 4.25; %Fuel value $/GJ
% mass flowrate kg/hr * 8.76 = MT/yr from AspenHysys
% fuel value produced from combustion as a fuel
% 8.76 -> MT/yr
Propylene_price = 11590*8.76*900;
propane_price = 11960*8.76*200;
H2_selling_price = 578.5*8.76*1400-25.2*8.76*1400;
Br2_purchase_price = 46340*8.76*3000-45860*8.76*3000;
% CO2_charge = 0.6172*311.1*44.01*8.76*40;
EP_max_P = Propylene_price-propane_price+H2_selling_price-Br2_purchase_price;
% catalyst cost
% sub-plant 1 hydrogenation catalyst
V_1 = 80000; % hysys reactor 2 volume in L
p_catalyst_1 = 140*0.88*0.5*V_1;
% sub-plant 2 dehydrobromination catalyst
V_2 = 120000; % hysys reactor 3 volume in L
p_catalyst_2 = 10*0.5*0.5*V_2;
EP_max_catalyst =  (p_catalyst_1 +  p_catalyst_2)*0.85;
```

J. Electrochemical Reactor Supplement

J.1 Theoretical Equations & Experimental Data

The minimum potential for the electrochemical reaction to occur is given by the Nernst Equation:

$$E = E^{\circ} - \frac{RT}{zF} \ln Q \text{ (J.1)}$$

Where E is the minimum potential, R is the ideal gas constant T is temperature, z is the ion charge, F is the Faraday constant, Q is the reaction quotient, and E° is the standard potential which is listed in Table J.1

Table J.1. Standard potential of anode and cathode in the electrochemical decomposition reaction.

Reaction	Standard Potential (V)
$Br_2 + 2e^{-} \rightleftharpoons 2Br^{-}$	1.087
$2H^{-} + 2e^{-} \rightleftharpoons H_2$	0

Based on Table J.1, the overall reaction has a standard potential of 1.087 (bromine reaction acts as the cathode and the hydrogen reaction acts as the anode). Using the Nernst Equation (equation J.2), a minimum potential of 1.093 V for an reactor at 25°C and 1.13 V for an reactor operating at 75 C are needed.

Besides the minimum potential, the overall current density and the faradaic efficiency (describing the efficiency with which charge (electrons) is transferred in a electrochemical system) are also key design variables. In this report, Alky Product Lmtd research group has provided the following experimental data:
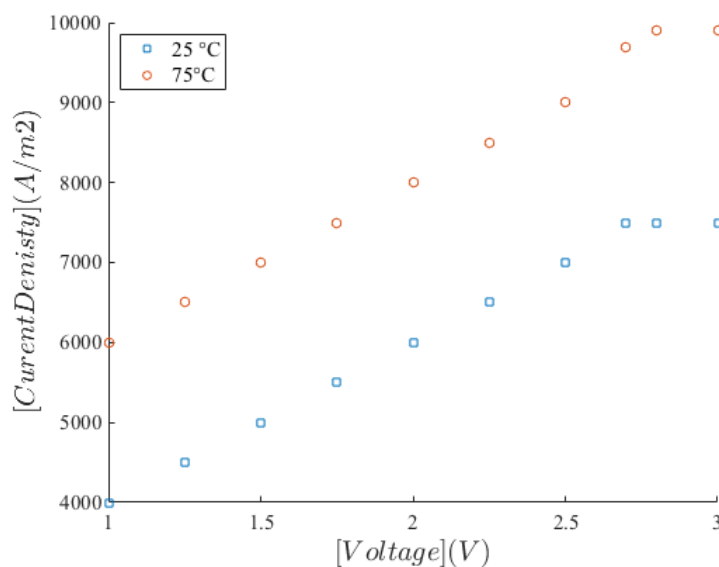
Figure J.1. Current Density data as a function of voltage at 25 °C and 75 °C in the electrochemical reaction
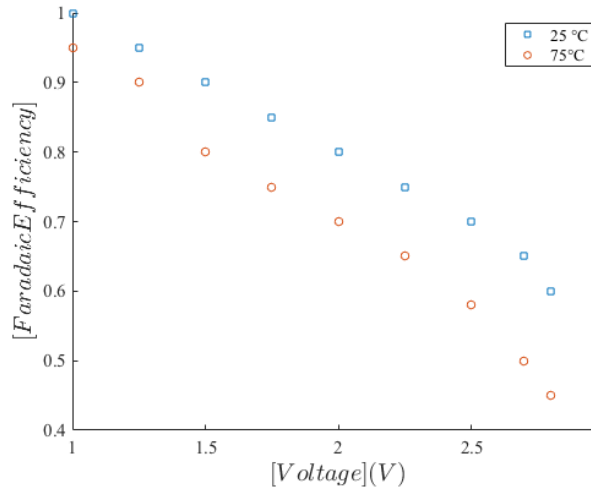
Figure J.2. Faradaic efficiency data as a function of voltage at 25°C and 75°C in the electrochemical reaction

Using this data, the capital cost and operating cost of an reactor are calculated in the following equation:

$$CapX = Installed\ Cost\ of\ Cell\ Subsystem\ and\ Power\ Unit\ +\ Installed\ Cost\ of\ the\ Reactor\ \text{(J.2)}$$

Which can be written as a function of current:

$$CapX = \frac{I}{A*e} * 10000\ \text{(J.3)}$$

Where I is the current, A is the current density, and e is the faradaic efficiency.

The operating cost can be written as:
$$OpX = I * V * Cost\ of\ Energy\ \text{(J.4)}$$
Where V is the voltage of the power system.

The minimum current needed for one year of operation was calculated by the following equation:

$$I = P_{Br_2} * z * 96485\ \text{(J.5)}$$

Where I is the current per year of operation. P_{Br_2} is the amount of bromine needed to be produced by the system. The ion charge (z) is 2.

J.2 Electrochemical Reactor MATLAB Code

```matlab
clear all
clc;
T=75+273.15;
FMHBr=408;%HBr in kta/year
FnHBr=(FMHBr*10^9)/(31556926*80.9119); %Mol HBr mol/s
PBr2=FnHBr/2; %Mol Br2 produced (mol/s)
MBr2=(PBr2*159.808*10^-3)*31556926; %Mass Br2 produced (kg/y)
Amp=PBr2*2*96485;
Ampy=(PBr2*2*96485)/(MBr2); %A/(kgBr2/y)
P=Ampy*((365*24)/1000); %V*n*(kwh/kgBr2)
dE=-1.09-((8.3145*T)/(96485.3321233*2))*log((PBr2^2)/(FnHBr)); %Minamuim Ecnomic Potential
%Experimental Data
V=[1,1.25,1.5,1.75,2,2.25,2.7,2.8,3]; %Voltadge
Va1=[4000,4500,5000,5500,6000,6500,7000,7500,7500,7500]; %25 C Voltdage Surface Efficahny
Va2=[6000,6500,7000,7500,8000,8500,9000,9700,9900,9900]; %75 C Votladdge Surface Efficahny
e1=[1,0.95,0.9,0.85,0.8,0.75,0.7,0.65,0.6,0.58]; %
e2=[0.95,0.9,0.8,0.75,0.7,0.65,0.58,0.50,0.45,0.4];
for i=1:length(V)
Preactor(i)=P*V(i);
Preactor2(i)=P*V(i)*.10^16;
OpX1(i)=MBr2*Preactor(i)*0.05;
A1(i)=Amp./(Va1(i).*e1(i));
CapX1(i)=A1(i)*10000;
end
for i=1:length(V)
Preactor(i)=P*V(i);
Preactor2(i)=P*V(i)*.10^16;
OpX2(i)=MBr2*Preactor(i)*0.05;
A2(i)=Amp./(Va2(i).*e2(i));
CapX2(i)=A2(i)*10000;
end
figure(1)
scatter(V,OpX1*10^-6,'filled','d')
hold on
scatter(V,OpX2*10^-6,'*')
hold off
a =gca; set(a,'Fontsize',15,'FontName','Times');%,'XTick',[0:0.1:0.8],'YTick',[-3:0.5:2]);
xl = xlabel('$[Voltage](V)$','interpreter','latex'); yl = ylabel('$[Cost](Million Dollars)$','interpreter','latex');
set(xl,'Fontsize',20,'FontName','Times');set(yl,'Fontsize',20,'FontName','Helvetica');
lgd = legend('25 °C','75°C','location','northwest');
lgd.FontSize = 15;

figure(2)
scatter(V,CapX1*10^-6,'filled','d')
hold on
scatter(V,CapX2*10^-6,'*')
hold off
a =gca; set(a,'Fontsize',15,'FontName','Times');%,'XTick',[0:0.1:0.8],'YTick',[-3:0.5:2]);
xl = xlabel('$[Voltage] (V)$','interpreter','latex'); yl = ylabel('$[Cost](Million Dollars) $','interpreter','latex');
set(xl,'Fontsize',20,'FontName','Times');set(yl,'Fontsize',20,'FontName','Helvetica');
lgd = legend('25 °C','75°C','location','northwest');
```

K. HAZOP Analysis

K.1 Reactor-1 HAZOP

Item	Study Node	Process Parameters	Guide Word	Possible Causes	Existing Safeguards	Action Required
1A	Reactor	Flow	No	• Clog in the feed pipes • Leak in the feed pipes • Leak in the reactor vessel • Clog in reactor vessel • Feed compressor/pump loss of power • Feed compressor/pump leak or failure • Feed compressor/pump clog • Critical power failure • PSA Failure	• Performing regular leak assessments. • Performing regular electrical/wiring assessments. • Regular quality assessments on the reactor product to assess any possible contaminate • Insulating the pipes • Using an corrosive resistant materials	• Stop all reaction operations • Contact Emergency Services • Use the secondary containment flair to discard all products • Seal all pipes leaving and coming from the reactor • Once the reactor clear performs an leak/clog assessment • Perform an electrical assessment • Restart the plant with the standard restart procedure. When restart the plant an unit safety analysis should be conducted
1B			High	• Too much reactants in the feed pipe • PSA failure	• Preprocess storge of all reactants • Controlled Flow addition of fluids to the reactant using valves and process control	• Lower the flow rate of the feed • Monitor for a possible sign of a pressure jump. If pressure increases too much, stop all reaction operations
1C			Lower	• Clog in the feed pipes • Leak in the feed pipes	• Performing regular leak assessments	• Perform a leak/clog assessment

	Guideword	Causes	Safeguards	Actions
		• Leak in the Reactor vessel • Clog in Reactor Vessel • Feed Compressor/pump loss of power • Feed Compressor/pump leak Feed Compressor/pump clog • Having too little feed	• Regular quality assessments on the reactor products to assess any possible contaminate • Insulating the pipes • Using corrosive resistant materials	• If flow rate in the feed pipes and in the feed is too low or there is rapid pressure drop, end all reactor operations Contact Emergency Services. Use the secondary containment flair to discard all products
1D	Part of	• Clog in the feed pipes • Leak in the feed pipes • Change in feed purity • Corrosion in the feed pipes • Feed contamination • PSA failure	• Performing semi regular feed quality testing • Performing corrosion assessments.	• In the case of a change in reactor composition it is important to maintain safe temperature and pressure levels. It may be useful to move to a different operating condition. • If the reactor composition is not manageable, stop all reaction operations
1E	Reverse	• Feed compressor/pump leak or failure • Feed compressor/pump power failure	• Performing regular leak assessments. • Using corrosive resistant materials • Performing regular electrical/wiring assessments	• Stop all reaction operations • Seal all pipes leaving and coming from the reactor • Perform an electrical assessment

ID	Parameter	Deviation	Causes	Prevention	Actions
1D		Other Than	• Clog in the feed pipes • Leak in the feed pipes • Change in feed purity • Corrosion in the feed pipes • Feed contamination	• Performing semi regular feed quality testings • Performing corrosion assessments	• Stop all reaction operations • Contact Emergency Services • Use the secondary containment flair to discard all products • Seal all pipes leaving and coming from the reactor • Once the reactor clear performs an contaminant assessment
2A	Temperature	Higher	• Clogging of the heating jacket • Heating jacket leak or block • Reactor contamination • Reactor pressure drop • Failure in temperature process control • Failure in pressure process control	• Performing regular leak assessments. • Having an secondary jacket cooling • Having secondary temperature process control • Using soft water in the heating jackets	• Activate the secondary cooling jacket • If continues stop all reaction operations • Contact Emergency Services • Use the secondary containment flair to discard all products • Access the process control
2B		Lower	• Increase Reactor Pressure • Reactor Leak • Feed contamination • Failure in Temperature process control • Failure in Pressure process control • PSA failure	• Using corrosive resistant materials • Having secondary temperature process control	• Lower the heating jacket duty • Lower the reaction pressure with the containment flair

ID	Parameter	Guide word	Causes	Safeguards	Actions
2C		Sooner	• Drop-in feed rate due to valve failure or leak • Failure in temperature process control	• Having secondary temperature process control • Performing regular leak assessments	• Use the secondary process control instruments to adjust the heating jacket • If needed use the emergency secondary cooling jacket
		Later	• Increase in the feed rate • Feed contamination	• Performing semi regular feed quality testing • Performing corrosion assessments	• Lower the heating jacket duty by lowering the amount of water is sent to the system
3A	Pressure	Higher	• Drop in temperature • Clog in reactor • Increase in the flow rate • Failure in temperature process control • Failure in pressure process control • Clog in reactor product stream	• Having secondary pressure process control • Having an safety valves for the feeds entering and leaving the process	• Use the secondary containment flair to discard some of the products • Lower the feed pump level • Lower the temperature of the reactor by lowering the duty of the heating jacket
3B		Lower	• Having a leak in the feed or reactor • Failure in temperature process control • Failure in pressure process control • Feed pump power failure • Feed pump mechanical failure	• Performing regular leak assessments. • Having secondary pressure process control • Insulating the pipes • Using corrosive resistant materials • Enclosing the reactor to the	• Switch to the secondary pump mechanism • If the pressure drops rapidly stop all reaction operations • Contact emergency services • Use the secondary containment flair to discard all products

ID	Parameter	Guideword	Causes	Prevention	Action
				• surrounding using cement • Having a secondary pump mechanism	• Seal all pipes leaving and coming from the reactor • Once the reactor clear performs an leak/clog assessment
3C		Sooner	• Clog in the reactor product stream • Increased Feed	• Performing semi regular feed quality testing • Performing corrosion assessments. • Having safety valves and secondary pressure relief mechanism	• Use the secondary containment flair to discard some of the products • Lower the heating duty on the jacket
3D		Later	• Feed pump power failure • Feed pump mechanical failure	• Having an secondary pump mechanism	• Switch to the secondary pump mechanism • If the pressure drops rapidly stop all reaction operations • Contact Emergency Services • Use the secondary containment flair to discard all products • Seal all pipes leaving and coming from the reactor • Once the reactor clear performs an leak/clog assessment
4A	Concentration	No	• Lack of flow • Clog in the feed pipes	• Performing regular leak assessments	• Stop all reaction operations

		Causes	Preventions/Safeguards	Actions
		• Leak in the feed pipes • Leak in the reactor vessel • Clog in reactor vessel • Feed compressor/pump loss of power • Feed compressor/pump leak or failure • Feed compressor/pump clog • Critical power Failure	• Performing regular electrical/wiring assessments. • Regular quality easements on the reactor product to assess any possible contaminate • Insulating the pipes • Using an corrosive resistant materials	• Contact Emergency Services • Restart the plant with the standard restart procedure. When restart the plant an unit safety analysis should be conducted
4B	Higher	• Too much feed • PSA failure	• Doing regular feed quality testing • Having recycle quality testing • Having an secondary process control on the PSA	• Close the gas recycle valve and bypass the PSA and send all the gas to the furnace • Switch to secondary gas pumps
4C	Lower	• Leak in the feed pipes • PSA failure	• Performing regular leak assessments. • Having secondary pressure process control • Insulating the pipes • Using corrosive resistant materials • Doing regular feed quality testing	• Perform a leak/clog assessment. • If flow rate in the feed pipes and in the feed is too low or there is a rapid pressure drop, end all reactor operations Contact Emergency Services. Use the secondary containment flair to discard all products • Close the gas recycle valve and bypass the PSA and send all the gas to the furnace

4E	Other Then	Feed contamination	• Doing regular feed quality testing	• Switch to secondary gas pumps
				• Continue to work as usual with monitoring temperature and pressure of the reactor
				• If temperature and pressure of the reactor go outside the safe operating conditions or of product, quality drops too low which ends all reactor operations
				• Restart the plant with the standard restart procedure. When restart the plant an unit safety analysis should be conducted
				• Consider switching feed suppliers

K.2 Distillation Column-1 HAZOP and MSDS

Item	Study Node	Process Parameters	Guide Word	Possible Causes	Existing Safeguards	Action Required
5A	Distillation Column-1	Flow	No	• Clog in the feed pipes • Leak in the feed pipes • Leak in the Distillation Column • Clog in Distillation Column • Critical Power Failure • Valve failure	• Preforming regular leak assessments. • Regular quality easements on the reactor product to assess any possible contaminate • Insulating the pipes • Having secondary safety valves	• Stop all distillation operations • Contact Emergency Services • Once the plant is clear performs an leak/clog assessment • Restart the plant with the standard restart procedure. When restart the plant an unit safety analysis should be conducted • Do an safety quality analysis on the flash drum
5B			High	• Flash drum failure • Flash drum too cold • Flash drum pressure leak • Reactor Temperature Too Low	• Preforming regular leak assessments. • Secondary process control on all unit ops	• Depending on the feed composition lower the reflux rate of the feed. • Monitor for an possible sign of an liquid height jump. If flooding in the reactor is too high stop reactor operations.
5C			Lower	• Clog in the feed pipes • Leak in the feed pipes • Leak in the distillation vessel •	• Preforming regular leak assessments. • Regular quality easements on the reactor product to assess any possible contaminate • Insulating the pipes	• Perform an leak/clog assessment. • If flow rate in the feed pipes and in the feed is too low or there is too much weeping lower the rate on the reboiler.

	Parameter	Deviation	Causes	Safeguards	Actions
				• Using corrosive resistant martials	
5D		Part of	• Clog in the feed pipes • Leak in the feed pipes • Change in feed purity • Corrosion in the feed pipes • Feed Contamination • Flash Drum failure	• Performing semi regular feed quality testing • Preforming corrosion assessments. • Having an secondary process control on the reactor	• Depending on the nature of the containment it may be useful to stop all reaction operations if the particle is small and the change of the feed is dependent quality wise it may be useful to recalibrate the boiler and reflux drum and increase or decrease the reflux and or boil up ratio.
6A	Temperature	Higher	• Feed contamination • Feed pressure drop • Flash drum clog • Reboiler clog or leak • Failure in Temperature process control • Failure in Pressure process control • Flash Drum Failure • Tray failure	• Performing regular quality and safety on the flash drum and reboiler. • Having secondary temperature process control	• Decrease the steam rate to the reboiler and or increase the cooling water to the condenser. • Decrease the distillation pressure • If continues and or extreme weeping is observed stop all reaction operations • Contact Emergency Services discard all products • Access the process control for an top down safety assement

ID			Causes	Prevention	Action
6B		Lower	• Increase Distillation Column Pressure • Distillation Column Leak • Feed contamination • Failure in Temperature process control • Failure in Pressure process control • Tray clogging or failure	• Using corrosive resistant martials • Having secondary temperature process control	• Increase the pressure of the distillation column. • Increase the steam rate to the reboiler and or decrease the cooling water to the condenser. • If continues and or extreme flooding is observed stop all reaction operations • Contact Emergency Services discard all products
7A	Pressure	Higher	• Increase in temperature due to reboiler failure and or reflux drum • Clog in the dilatation column • Failure in Temperature process control • Failure in Pressure process control • Flash drum failure	• Having an safety valves for the feeds entering and leaving the process • Performing regular quality and safety on the flash drum and reboiler.	• Change the operating conditions of the reboilers and or condenser • Change the flash drum operating conditions • If the problem prosaists end distillation operations and perform and top down safety analysis
7B		Lower	• Having an leek in the feed or distillation drum • Failure in the falsh drum • Decrease in temperature due to reboiler failure and or reflux drum • Failure in Temperature process control • Failure in Pressure process control	• Preforming regular leak assessments. • Having secondary pressure process control • Insulating the pipes control • Using corrosive resistant martials • Having an secondary pump mechanism	• Switch to the secondary pump mechanism • Perform an safety assessment on the flash drum. • If the pressure drops rapidly stop all distillation operations • Contact Emergency Services

					• Having seconder pressure process control	• Use the secondary containment flair to discard all products • Seal all pipes leaving and coming from the distillation column.

Team Member Work Statement

Michael Xing

I did most of the data analysis, writings, Hysys designs, and everything associated with this project.

Selina Liu

Revised the balances on process design, wrote Matlab code, made NPV calculation spreadsheet and sencitvity analysis. Wrote the report.

Yunus Ross

Wrote the Statement of process chemistrand process diagrams and program files for the level 2. Helped to create the MATLAB level 2 flow sheet and economic balance Made the HAZOP analysis for PFR-1. Did the safety research and calculations.

Print Name and Sign: _____Langqi Xing_____   Date: _____06/01/2022____

Print Name and Sign _____Selina Liu_____   Date: ___06/01/2022_____

Priname and Sign _____Yunus Ross_____   Date: ___06/01/2022_____

Rating of Team Members for Design Project

Please rate each group member's contributions in the categories below:
1-2 - unsatisfactory, 3 - acceptable/adequate, 4 – very good, 5 - excellent
Each member fills out one form and signs the bottom.

Name   : 1) ____Michael Xing_____   2) ___Yunus Ross_____   3) _____Selina Liu_____

	1) Michael Xing	2) Yunus Ross	3) Selina Liu
Quality of work presented	__5___	___4__	___5__
Quantity of work performed	___5__	___4__	__5___
Effort	__5___	__5___	__5___
Punctuality (meetings and deadlines)	___5__	__5___	__5___
Knowledge of design methods	___5__	__5___	__5___
Class attendance	__5___	__5___	__5___
Communication	__5___	__5___	__5___

Do you feel that each member of the group deserves the same grade? If not, who does not and why?

Yes, each member of the group deserves the same grade.

It's important to note that differences in performance will not necessarily affect individual grades; however, large discrepancies may result in differences in grades.

Additional comments:

Print Name and Sign: _____Langqi Xing_____ Date: _____06/01/2022_____

Rating of Team Members for Design Project

Please rate each group member's contributions in the categories below:
1-2 - unsatisfactory, 3 - acceptable/adequate, 4 – very good, 5 - excellent
Each member fills out one form and signs the bottom.

Name : 1) ____Langqi Xing_____   2) ___Yunus Ross_____   3) _____Selina Liu_____

Quality of work presented	__5___	___4__	___5__
Quantity of work performed	___5__	___4__	__5___
Effort	__5___	__5___	__5___
Punctuality (meetings and deadlines)	___5__	__5___	__5___
Knowledge of design methods	___5__	__5___	__5___
Class attendance	__5___	__5___	__5___
Communication	__5___	__5___	__5___

Do you feel that each member of the group deserves the same grade? If not, who does not and why?

Yes, each member of the group deserves the same grade.

It's important to note that differences in performance will not necessarily affect individual grades; however, large discrepancies may result in differences in grades.

Additional comments:

Print Name and Sign: _____Selina Liu_____ Date: _____06/01/2022____

Rating of Team Members for Design Project

Please rate each group member's contributions in the categories below:
1-2 - unsatisfactory, 3 - acceptable/adequate, 4 – very good, 5 - excellent
Each member fills out one form and signs the bottom.

Name : 1) ____Michael Xing_____   2) ___Yunus Ross_____   3) _____Selina Liu_____

	1) Michael Xing	2) Yunus Ross	3) Selina Liu
Quality of work presented	__5___	___5__	___5__
Quantity of work performed	___5__	___4__	__5___
Effort	__5___	__5___	__5___
Punctuality (meetings and deadlines)	___5__	__5___	__5___
Knowledge of design methods	___5__	__4___	__5___
Class attendance	__5___	__5___	__5___
Communication	__4___	__5___	__4___

Do you feel that each member of the group deserves the same grade? If not, who does not and why?

Yes, each member of the group deserves the same grade.

It's important to note that differences in performance will not necessarily affect individual grades; however, large discrepancies may result in differences in grades.

Additional comments:

Print Name and Sign: _____Yunus Ross_____ Date: _____06/01/2022_____