16, April 2021

AIChE 2020-2021 Student Design Competition

Design Project Team, "LADS"

The following document is provided to AIChE Student Programs in response to the issuance of the AIChE 2020-2021 Student Design Competition by student design team LADS. Attached is a preliminary study estimate for a catalytic reforming unit retrofitting for a toppings refinery owned and operated by a Mr. Abbasi, for the purpose of further processing fuels to meet refining standards typical of western countries This study proposes a design estimate for this addition with an accompanying economic analysis, under the conditions of either Kurdish or Iraqi taxation, for the consideration of Mr. Abbasi.

LADS is prepared to address any additional questions or concerns that concerning this submission and the contents therein.

Regards,

LADS

AIChE 2020-2021

Student Design Competition

Toppings Refinery Retrofit

Study Estimate

Executive Summary

The Iraqi government has recently been closing smaller refineries with inadequate process safety, operational standards, and plant efficiency in an effort to advance toward Western refining standards. Mr. Abbasi currently runs a small toppings refinery in Kirkuk, Iraq, that he fears could get shut down if he does not begin to separate benzene from the plant's fuel products. A study estimate has been conducted to evaluate the economic viability of a fixed bed catalytic reformer unit that would connect to Mr. Abbasi's small topping refinery to process naphtha into separate gasoline, benzene, toluene, and xylene product streams.

The study estimate predicts this project to be exceptionally economically attractive and recommends that the project enter the next stage of design. An economic analysis estimate of the project finds the toppings refinery retrofit, based on Iraqi taxes and feed condition of K, produces annual revenue of $191.1 million, with a fixed capital investment of $64.1 million, expected annual operating costs of $11.5 million, and working capital totaling $9.6 million. These estimates produce a net present value (NPV) of $113.3 million, an impressive discounted cash flow rate of return (DCFROR) of 47%, and a reasonable payback period of 2.59 years. Considering the volatility of oil and gas markets, there is a small chance that this project could become unattractive if revenues vary negatively by 20%, but this is only the case for feed K and Iraqi taxes.

The three subunits that make up the toppings refinery retrofit include a reactor section, an extraction section, and a distillation section. The reactor section takes the naphtha feed containing large amounts of benzene, cyclohexane, and n-decane, heats it, and then sends the hot feed through 3 packed bed reactors. The reactors are filled with a platinum catalyst on alumina support. The lighter products are recycled at a rate of 10% while the rest are purged to be used for facility operations. The heavier products are sent to the extraction section. Here, sulfolane is used to strip medium to heavy hydrocarbons from the BTX components in a liquid-liquid extractor. The sulfolane is then recovered from each stream and recycled back through. The third section distills the BTX into its three main components, benzene, toluene, and para-xylene.

Due to the nature of the process and the concerns associated with government shutdowns, establishing a strong safety culture is of the utmost importance. As a result of the large amount of highly flammable materials involved in this process, it is recommended that all workers wear flame resistant clothing, hard hats, and shatterproof safety glasses when within 1025 m of the major fractionator. Buildings should not be built within 152 m of the major fractionator, and gas leak detection systems should be placed throughout the plant.

When considering whether or not a fixed bed catalytic reformer unit in Mr. Abbasi's situation should be recommended for the next design stage, one should not only consider the volatile markets associated with this unit, they should also recognize what could happen if he chooses to do nothing. This argument is why the recommendation for the advancement of this project is a strong one. Another recommendation is that heat integration should be used to preheat the feed before the first furnace pass, using the hot stream exiting the reactor section and hot sulfolane located in the extraction section to increase efficiency and lower costs.

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Brief Process Description

Introduction

Intent of Process and Design Philosophy

The design project team proposes a fixed bed continuous catalytic reformer and downstream separation unit with the goal of treating naphthas fed to Mr. Abbasi's refinery to convert toxic cycloalkanes and polyaromatic compounds to mono aromatics, upgrade the octane of linear alkanes, and refine these treated naphthas to produce gasoline, diesel, and salable aromatics. This unit produces products adhering to refining standards typical of western countries, concerning the aromatics composition of fuels. The unit ensures that Mr. Abbasi's refinery will continue to be in line with Iraqi refining standards in the future and produces revenues from otherwise undesirable components present in feed naphthas.

The process is designed with the goal of minimizing the presence and extent of high-risk conditions and equipment, as well as minimizing the risks associated with this equipment. In addition, the design opts to incorporate additional equipment to recover costs associated with the operation of equipment requiring large utility purchases, specifically large furnaces and heat exchangers. The addition of equipment, and complication of the process and its operation, is deemed acceptable when risks associated with the equipment to be added are low, potential savings are high, and/or when additional equipment will reduce the extent of or risks associated with other equipment. This design is not principally concerned with limiting equipment or the number of operators required to monitor and maintain it and is instead concerned with limiting the impact of failure and difficulty of maintenance for individual pieces of equipment.

Major Feeds and Products Summary

The process has one major feed, naphtha, one minor feed, water, and four salable products: a mixture of gasoline and diesel fuels, which can be further processed to produce gasoline and diesel adherent to western refining standards, benzene, toluene, and xylenes. These streams flowrates, conditions, and compositions are summarized in Table 1. The process produces three non-salable products: a light gas rich in hydrogen, methane, and ethane, a light gas rich in ethane, propane, and butane, and (low pressure) steam. These non-salable products are delivered to other areas of the refinery to serve as reactants or utilities in other processes. These streams flowrates, conditions, and compositions are summarized in Table 2.

The process has a feed and product of sulfolane for the extraction section, summarized below and described in detail in the Extraction Section Detail appendix. This sulfolane is not consumed by the process and is instead continuously recycled. However, over time, the quality and amount of this sulfolane diminishes due to small impurities in treated sulfolane and minor losses of sulfolane in product streams, eventually requiring replacement.

Table 1. Major Feed and Product Streams (Feed K)

Stream	Naptha	Fuel	Benzene	Toluene	Xylenes
Major Feed and Product Streams (Feed K)					
Mass Flow (kg/hr)	34,800	18600	2660	3530	2490
Volume Flow (BPD)	7000	4080	455	612	435
Temperature (°C)	70	35	80	113	166
Pressure (kPa)	120	150	108	108	200
Composition (vol %)					
C_1-C_4	0	0.3	0	0	0
C_5-C_8	0	73.2	0	0	0
C_9-C_{10}	73.6	26.4	0	0	0
Cycloalkanes	21.4	0.04	0	0	0
Benzene	5	0.08	99.9	0.1	0.9
Toluene	0	0	0.1	98.9	99.1
Xylenes	0	0	0	1	0
Other	0	0.02	0	0	0

Table 2. Minor Feed and Product Streams (Feed K)

Stream	Water	Non-Condensable	Light Gas	Steam
Minor Feed and Product Streams (Feed K)				
Mass Flow (kg/hr)	1,080	3820	4910	1080
Volume Flow (m³/hr)	1.1	678	1620	1725
Temperature (°C)	35	35	39	102
Pressure (kPa)	150	495	148	108
Composition (Mole %)				
Hydrogen	0	9.6	0.1	0.00
C_1-C_4	0	86.0	81.9	0.00
C_5-C_8	0	3.0	12.7	0.00
C_9-C_{10}	0	0.1	0.1	0.00
Cycloalkanes	0	0.0	0.0	0.00

Aromatics	0	1.3	5.2	0.00
Water	1	0.0	0.0	99.99
Other	0	0.0	0.0	0.01

Overall Process Summary

Naphtha fed to the unit enters the **reactor section**, which converts component cycloalkanes and polyaromatics to monoaromatics (here forward referred to as aromatics) and upgrades the octane of component linear alkanes. This processed feed is separated to produce a non-condensable gas stream rich in hydrogen, methane, and ethane, a light gas stream rich in ethane, propane, and butane, and a light liquid mixture consisting of aromatics, gasoline, and diesel, the extraction section feed.

The extraction section feed, water, and extraction solvent, sulfolane, enter the **extraction section**, which separates feed component gasoline and diesel from aromatics. This section produces a mixture of diesel and gasoline, a small purge of recovered sulfolane, steam, and a stream rich in aromatics with some linear alkanes, the distillation section feed.

The distillation section feed enters the **distillation section** which separates remaining linear alkanes from aromatics, and further separates aromatics into benzene, toluene, and xylenes. This section produces salable products of pure benzene, pure toluene, and pure xylenes. This section also produces a light liquid rich in benzene and linear alkanes, and a light gas rich in benzene and linear alkanes, both of which are recycled back to the extraction section.

Abbreviated descriptions of each section are below, with detailed descriptions and relevant information in the Reactor Train Detail, Extraction Section Detail and Distillation Section Detail. Process Flow Diagrams for each section are in Figure 1, Figure 2, and Figure 3.

Figure 1.
Reaction Section PFD
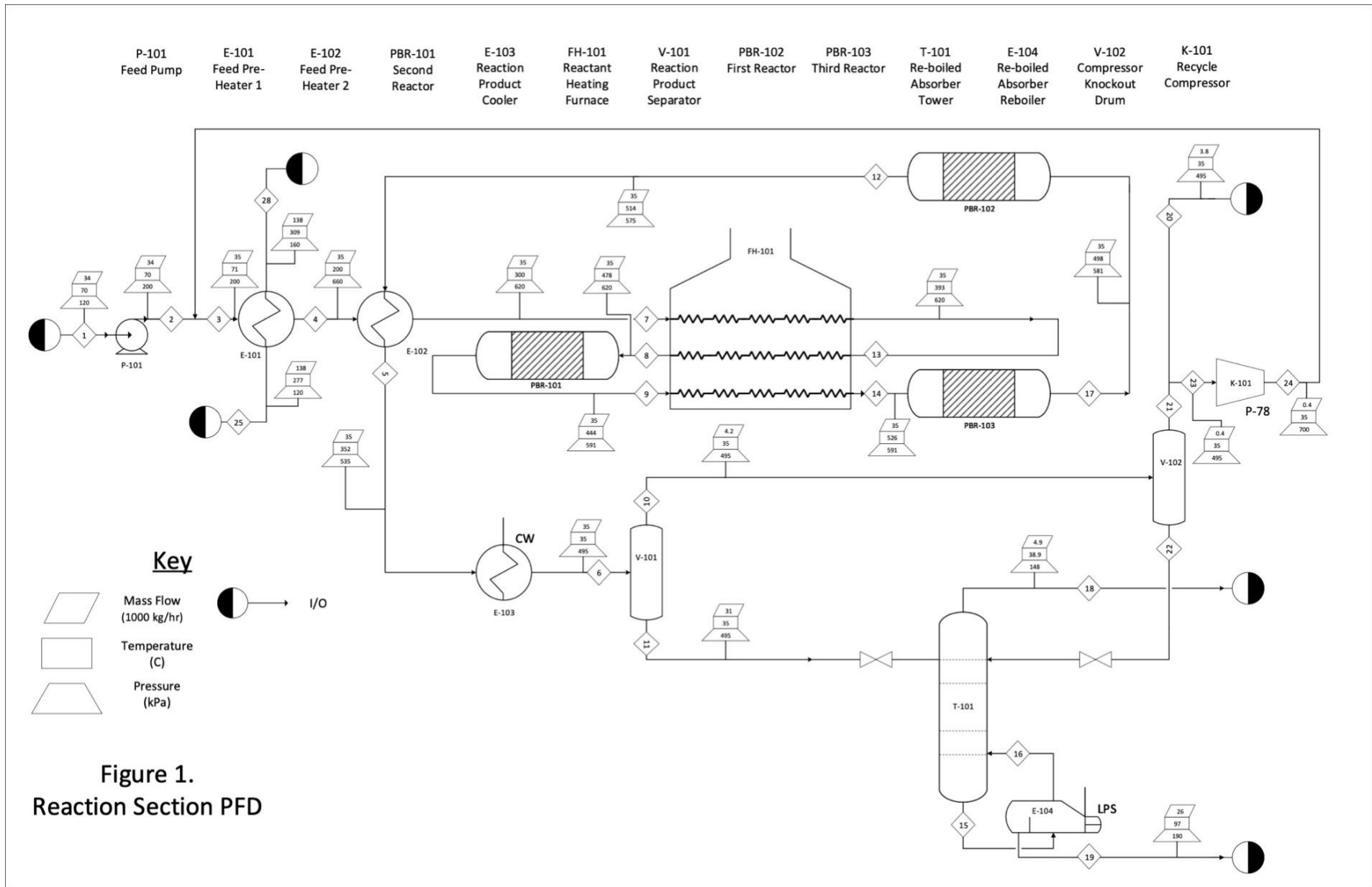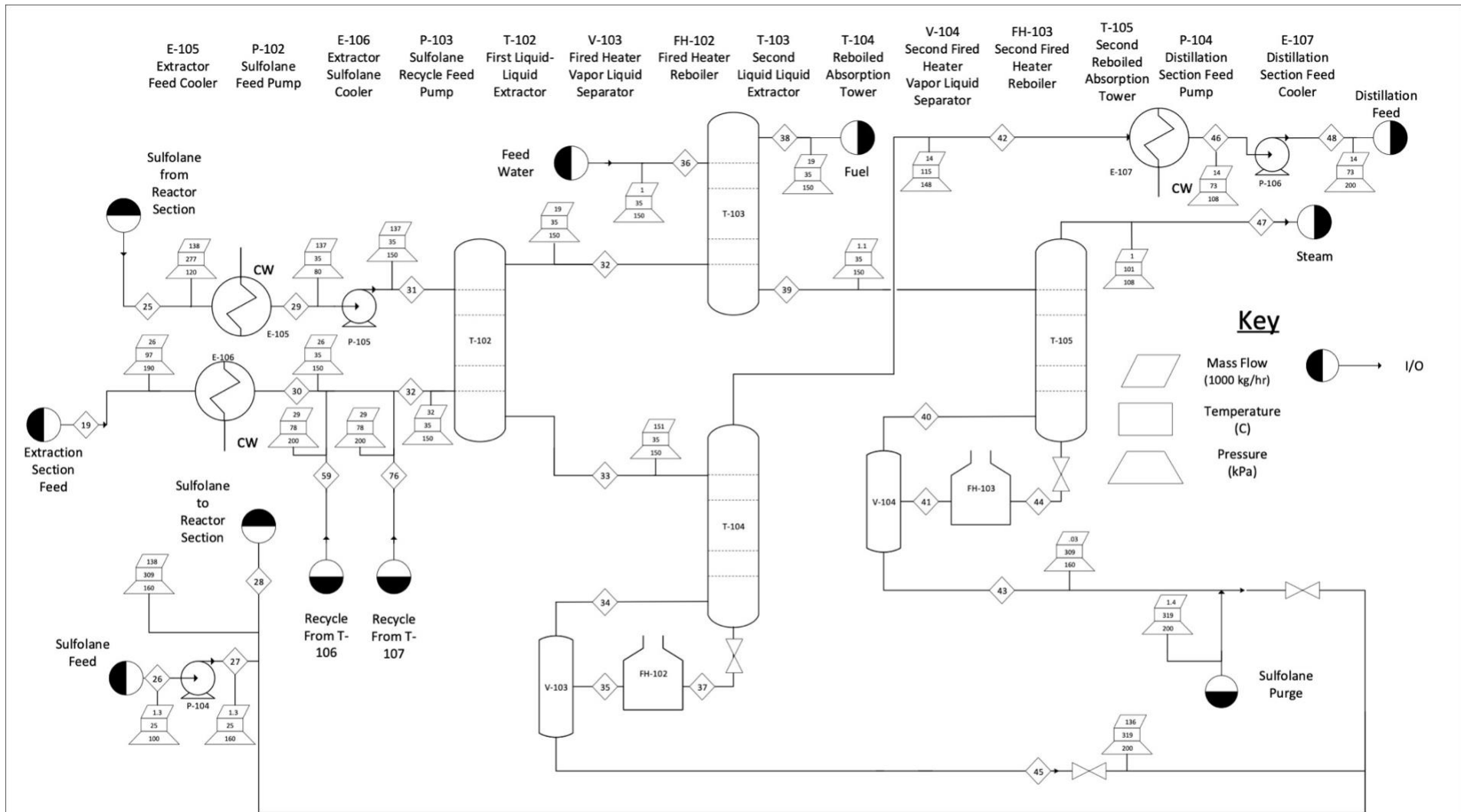
Figure 2.
Extraction Section PFD
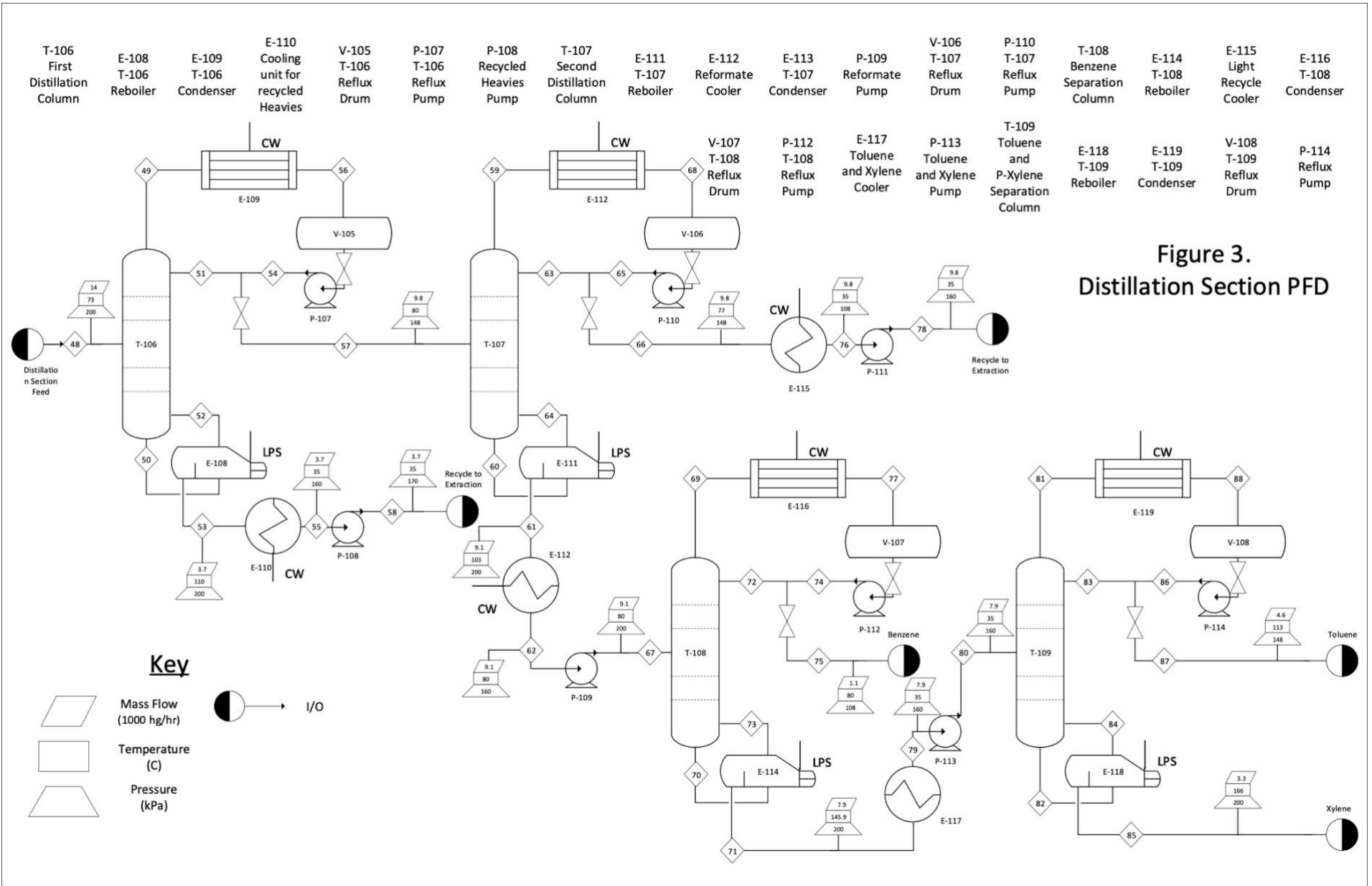
Figure 3.
Distillation Section PFD

Key

Mass Flow (1000 hg/hr)

Temperature (C)

Pressure (kPa)

I/O

Economic Analysis and Sensitivities

Capital Cost Estimates

The calculated costs for all units in the process utilize values taken from the GPSA handbook[6], Turton et al.[13], and Seider et al[11]. Project construction will begin in 2022, therefore the capital costs will be applied in the same year. Capital costs will be on a 10-year MACRS depreciation for a 5-year project life spanning from 2022 to 2027. The total for the capital cost is calculated after sizing equipment for both naphtha streams provided and using the larger equipment between the two. Table 3 shows the capital cost breakdown by unit for the project life. The project's most expensive component was the catalyst required for the reaction section, which is a one-time purchase of $55,395,000. In Figure 4 the percentages of capital costs are broken down into their respective categories, showing that the heat exchangers make up 50% of the total capital costs.

Table 3. Equipment Capital Cost Breakdown

Equipment	Cost
Distillation Columns and Trays	$ 582,000
Distillation Reflux Pumps	$ 101,000
Distillation Reflux Drums	$ 94,000
Heat Exchangers (stand-alone)	$ 3,563,000
Heat Exchangers (Condensers)	$ 649,000
Heat Exchangers (Reboilers)	$ 2,260,000
Absorption Columns and Trays	$ 330,000
LL Extractors and Packing	$ 367,000
Reactors	$ 441,000
Compressor	$ 184,000
Separators	$ 1,516,000
Pumps	$ 368,000
Fired Heaters	$ 3,405,000
Total Costs	**$ 14,819,000**
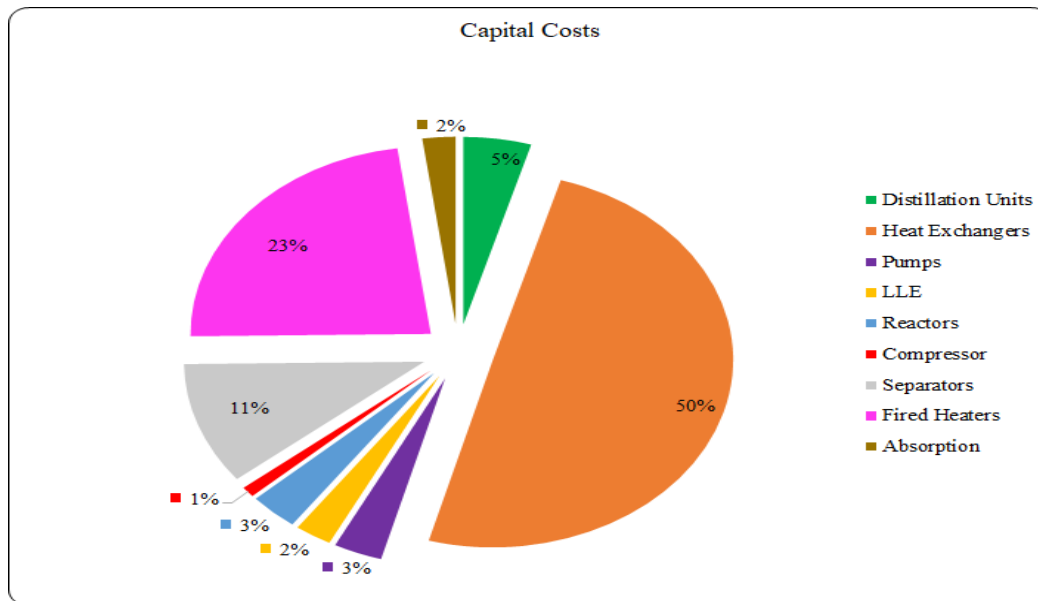
Figure 4. Capital Cost Breakdown

Operating Costs, Material Costs, and Revenue

Operating costs are a combined cost consisting of utility costs, labor costs, direct supervisory costs, maintenance costs, and operating supplies. Utility costs associated with the process are calculated from the parameters of the heat exchangers, compressor, pumps, fired heaters, and service costs. Values are given for the cost of utilities by AIChE. Stand-alone heat exchangers, condensers, fired heaters, and the compressor utility costs are calculated using the duty of the exchangers, while the reboilers are calculated by the steam rate per exchanger. The compressor and pumps utility costs are calculated using the purchased kW of each unit. Labor costs are calculated using eqn. 1 which calculates the cost for the operating personnel. Where N_{np} is the quantity of equipment without the pumps or vessels, P is the total processing steps, and N_{oL} is the total operators per shift. This project requires a minimum number of 18 total operators being paid $7.18 per hour [4] which is 4.38 times less than American wages. The remaining operating costs are calculated from equations in chapter 8 of Turton et al. In Figure 5 and Figure 6 the total operating costs are broken down by stream to illustrate where the bulk of the operating costs stem from.

$$N_{oL} = (6.29 + (31.2 * P^2) + (0.23 * N_{np}))^{.5} \tag{1}$$
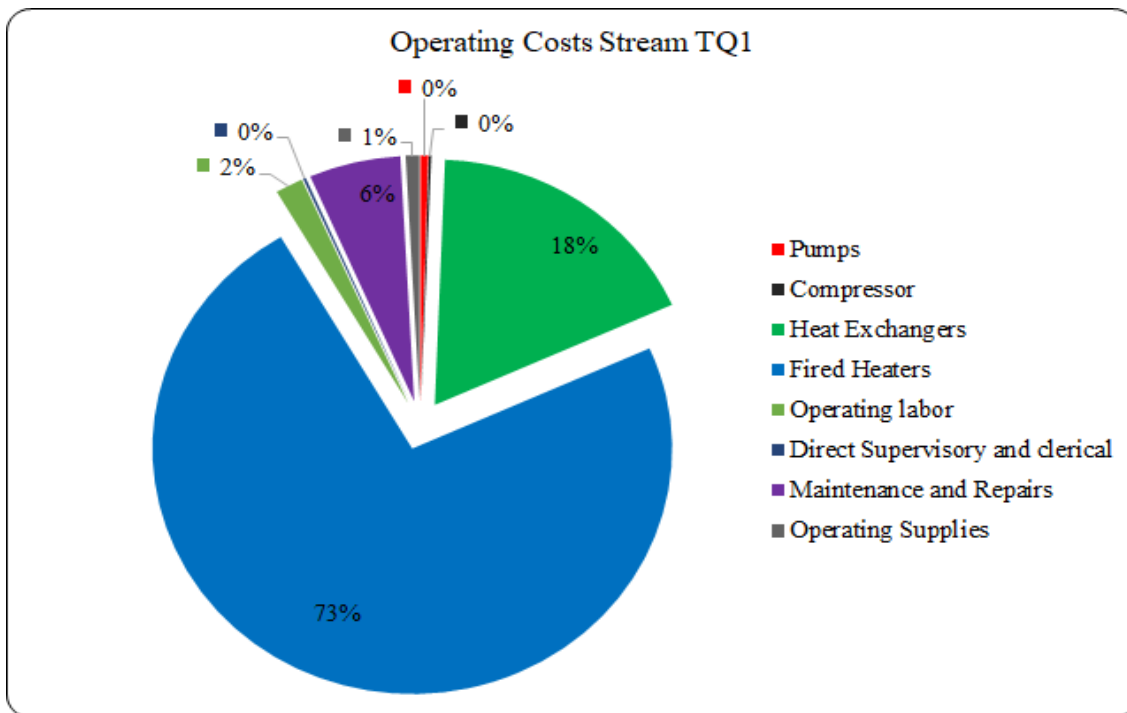
Figure 5. Operating Costs for Stream TQ1
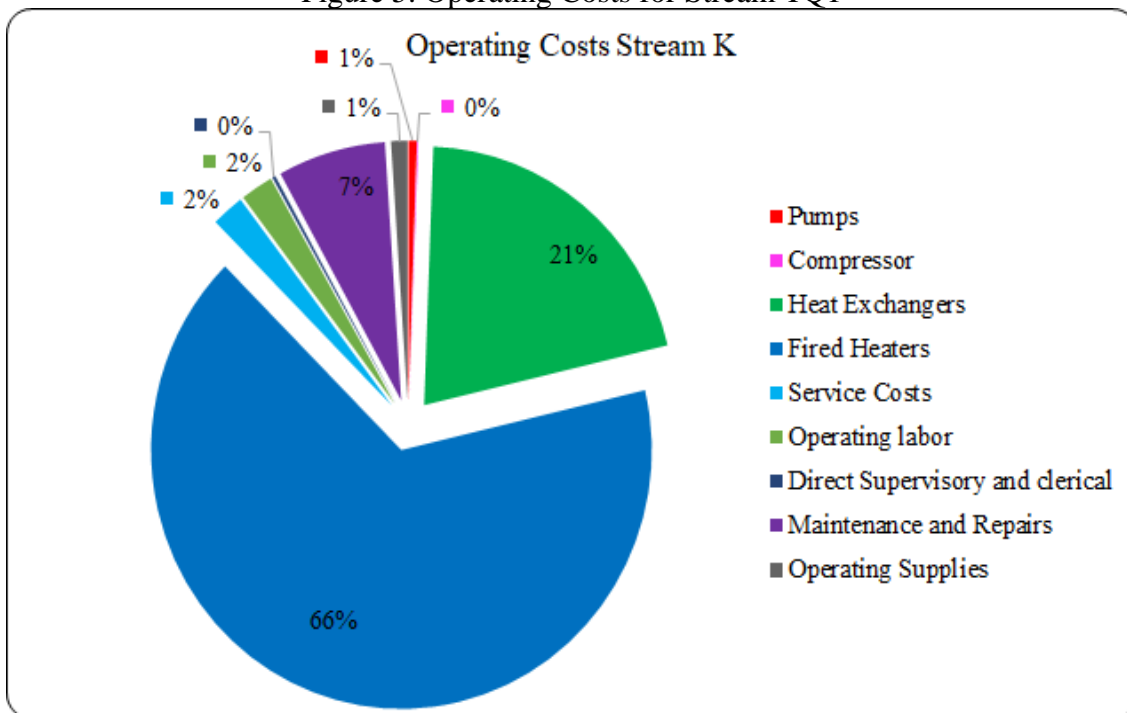
Figure 6. Operating Costs for Stream K

Comparing Fig. 5 and 6 it is clear that stream TQ1 has a larger portion of the operating costs consisting of the fired heaters utility costs. This is expected as TQ1 has a higher naphtha flow rate compared to K. The overall total operating costs for stream TQ1 and K are $15,606,000 and $12,493,000 respectively.

The material costs for this project are calculated from the amount of naphtha for each stream. Values to calculate these costs are given by AIChE. The naphtha cost is determined by taking the percent volume of crude and multiplying it by the crude volumetric flow, this is then multiplied by the

cost of naphtha per liter. Stream K has a yearly naphtha cost of $99,080,000 while stream TQ1 has a yearly naphtha cost of $138,712,000.

Revenues for the project consist of 5 components: benzene, toluene, para-xylene, gasoline, and diesel sales. Benzene, toluene, and para-xylene are the final products of the distillation section and are directly sold at a 99% purity. The gasoline and diesel sales are calculated by taking the molar flows of each component associated with the gasoline and diesel from the purge stream. Stream K and stream TQ1 will have different revenue values due to the flow and composition of naphtha being brought into the system. Table 4 and 5 show the revenue values for stream K and TQ1 respectively. As seen in the tables, the revenue of the project using naphtha stream TQ1 produces a much higher revenue while having a higher cost for the naphtha.

Table 4. Yearly Production Revenue for Stream K

Component	Price (2021)	Unit	Yearly Production	Revenue
Benzene	3.49	$/gal	212.4	$ 24,360,000
Toluene	2.792	$/gal	803.3	$ 26,097,000
Para-Xylene	2.792	$/gal	570.5	$ 18,556,000
Gasoline	0.63	$/Liter	1.42E+08	$ 81,610,000
Diesel	0.98	$/Liter	4.54E+07	$ 40,459,000
			Total	**$ 191,082,000**

Table 5. Yearly Production Revenue for Stream TQ1

Component	Price (2021)	Unit	Yearly Production	Revenue
Benzene	3.49	$/Gal	371.6 Gal	$ 11,361,000
Toluene	2.792	$/Gal	1406 Gal	$ 34,388,000
Para-Xylene	2.792	$/Gal	998.3 Gal	$ 24,416,000
Gasoline	0.63	$/Liter	2.07E+08 Liter	$ 119,111,000
Diesel	0.98	$/Liter	7.52E+07 Liter	$ 67,037,000
			Total	**$ 256,318,000**

DCFROR Analysis

The project economics consisted of a hurdle rate of 15% and 2 separate tax rates due to the disputed territory of the location of the process. For the analysis a 5-year project life was chosen as well as a 10-year MACRS depreciation for the equipment and working capital. Depreciation was calculated for working capital due to it consisting of the catalyst and sulfolane which are used for the process. The depreciation for capital costs starts in 2023 while depreciation for working capital starts in 2024. Purchase costs will take place in 2022 with production starting in 2023 with a working capital applied in

2022 to account for catalyst and sulfolane purchase. Table 6 shows the economic template used for each tax rate as well as the different streams. The project will have 2 NPVs and DCFRORs for each stream that the economic analysis is based on. Both streams produce a maximum net present value (NPV) and discounted cash flow rate of return (DCFROR) under the Kurdish tax rate. TQ1 has a maximum NPV of $227,420,000 and DCFROR of 91% while K has a maximum NPV of $164,924,000 and DCFROR of 72%. Minimum values for these streams are NPVs of $164,335,000 and $119,314,000 as well as DCFRORs of 66% and 53% respectively. This shows that in each case under each tax rate the project is economically feasible, as the DCFROR values are always greater than the minimum rate of return. For this project, a service factor of 91% is assumed when calculating revenue and operating costs to account for downtime where the process is not running. In this analysis an undiscounted and discounted payback period for K and TQ1 are calculated under both tax rates. Stream K will have undiscounted payback periods for Iraq tax rates and Kurdish tax rates of 2.29 and 1.99 respectively. The discounted payback periods for K are 2.49 and 2.14 respectively. Stream TQ1 will have undiscounted payback periods of 2.08 and 1.82 respectively and discounted payback periods of 2.25 and 1.94 respectively. Initial capital cost of the project totals $14,819,000 and a working capital in 2022 of $57,617,000. Capital cost is determined by costing each piece of equipment in the process and working capital is 15% of the capital cost plus the sulfolane and catalyst cost. The raw material costs consist of the yearly naphtha cost based on values for feed K provided by AIChE. Write off in year 5 is the remainder of the depreciation for both capital and working capital costs. Cash flow values represent the amount of money incurred in a single year, while discounted cash flow values represent the present dollar value in 2022.

Table 6. Cash Flow Table for Stream K with Iraq Tax Rates

End of Year	2022	2023	2024	2025	2026	2027
Sales Revenue	-	191,081,880	191,081,880	191,081,880	191,081,880	191,081,880
Net Revenue	-	191,081,880	191,081,880	191,081,880	191,081,880	191,081,880
[-] Raw Material Costs	-	(99,080,008)	(99,080,008)	(99,080,008)	(99,080,008)	(99,080,008)
[-] Other Op Costs	-	(12,492,844)	(12,492,845)	(12,492,845)	(12,492,845)	(12,492,845)
[-] Depreciation	-	(1,481,948)	(7,933,262)	(11,612,365)	(9,289,892)	(7,432,507)
[-] Writeoff	-	-	-	-	-	(29,727,063)
Taxable Income	-	78,027,079	71,575,765	67,896,662	70,219,135	42,349,458
[-] Tax @ 35%	-	(27,309,478)	(25,051,518)	(23,763,832)	(24,576,697)	(14,822,310)
Net Income	-	50,717,601	46,524,247	44,132,830	45,642,438	27,527,148

[+] Depreciation		1,481,948	7,933,262	11,612,365	9,289,892	7,432,507
[+] Writeoff	-	-	-	-	-	29,727,063
[-] working Capital	(52,657,555)		-	-	-	-
[-] Capital Cost	(14,819,483)	-				
Cash Flow	(67,477,038)	52,199,550	54,457,510	55,745,196	54,932,330	64,686,717
Discount Factor (P/Fi*,n)	1.0000	0.8696	0.7561	0.6575	0.5718	0.4972
Discounted Cash Flow	(67,477,038)	45,390,913	41,177,701	36,653,371	31,407,738	32,160,731
NPV @ i* =	119,313,415	"NPV > 0, Economically Attractive"			**PWNet Costs**	(67,477,038)
DCFROR =	53%	"DCFROR > 0, Economically Attractive"				
Benefit Cost Ratio =	6.40	"PWNet Costs < NPV, Economically Attractive"				
ROR =	75%	"ROR > i*, Economically Attractive"				

Sensitivity analysis is done across four parameters: capital costs, operating costs, product revenue, and raw material costs. A 20% increment is used with each of these parameters to determine the economic flexibility of the project. Table 7 displays the sensitivity analysis by showing the new values as well as the base case for stream K under Iraq tax rates. As seen in Table 7 the base DCFROR and NPV are 53% and $119,310,000 respectively. Change in DCFROR is calculated using Eqn. 2 and change in NPV is calculated using Eqn. 3. The largest change in DCFROR is associated with the product revenue. Increasing revenue 20% gives a DCFROR of 86% and decreasing product revenue gives a DCFROR of 17%. This shows that the lowest rate of return achievable is still above the required minimum rate of return according to the sensitivity analysis. Values in Table 7 are calculated using the Iraq tax rate of 35%. Switching to the Kurdish tax rate of 15% will only increase our DCFROR values across the board as well as the NPV. Figures 7-14 show the results of the sensitivity analysis for K and TQ1 under Iraq and Kurdish tax rates. From these figures it is clear that the greatest factor in the project's economic feasibility is the product revenue. Revenue is followed by material costs, operating costs, and capital costs in order of importance for each figure. The only factors that switch positions throughout the figures are the operating costs and capital costs. These are also the two least important due to the lack of change they cause in the DCFROR and NPV. Therefore, this project has a very high flexibility when considering the effects of operating and capital costs on the economic feasibility. In all

eight of the figures the NPV never reaches zero and the DCFROR never reaches 15%. Therefore, this project is economically feasible and flexible.

$$Change\ in\ DCFROR = \frac{New\ DCFROR - Old\ DCFROR}{Old\ DCFROR} * 100 \qquad (2)$$

$$Change\ in\ NPV = \frac{New\ NPV - Old\ NPV}{Old\ NPV} * 100 \qquad (3)$$

Table 7. Sensitivity Analysis for Stream K with Iraq Tax Rates

Capital Costs	% Change	New Investment	DCFROR	NPV	Change ROR	Change NPV
$ (14,820,000)	(+) 20%	$ (17,784,000)	49%	$ 116,630,000	-6.40	-2.25
$ (14,820,000)	Base Case	$ (14,820,000)	53%	$ 119,310,000	0.00	0.00
$ (14,820,000)	(-) 20%	$ (11,856,000)	56%	$ 122,000,000	7.03	2.25
Operating Cost	% Change	New Op Costs	DCFROR	NPV	Change ROR	Change NPV
$ (12,490,000)	(+) 20%	$ (14,988,000)	50%	$ 113,880,000	-4.23	-4.55
$ (12,490,000)	Base Case	$ (12,490,000)	53%	$ 119,310,000	0.00	0.00
$ (12,490,000)	(-) 20%	$ (9,992,000)	55%	$ 124,760,000	4.23	4.57
Product Revenue	% Change	New Product Revenue	DCFROR	NPV	Change ROR	Change NPV
$ 191,080,000	(+) 20%	$ 229,296,000	86%	$ 202,580,000	63.44	69.79
$ 191,080,000	Base Case	$ 191,080,000	53%	$ 119,310,000	0.00	0.00
$ 191,080,000	(-) 20%	$ 152,864,000	17%	$ 36,040,000	-67.49	-69.79
Raw Material Cost	% Change	New Material cost	DCFROR	NPV	Change ROR	Change NPV
$ (99,080,000)	(+) 20%	$ (118,896,000)	35%	$ 76,140,000	-34.16	-36.18
$ (99,080,000)	Base Case	$ (99,080,000)	53%	$ 119,310,000	0.00	0.00
$ (99,080,000)	(-) 20%	$ (79,264,000)	70%	$ 162,490,000	33.17	36.19
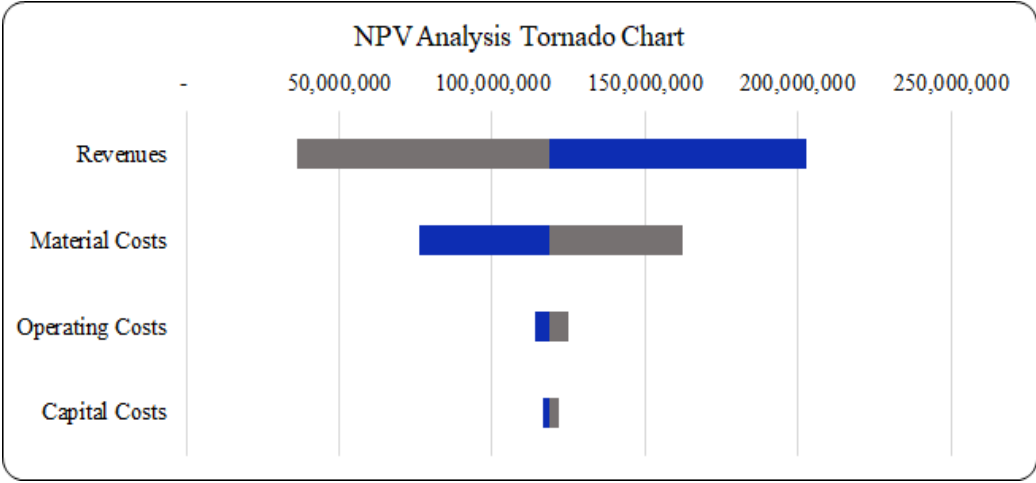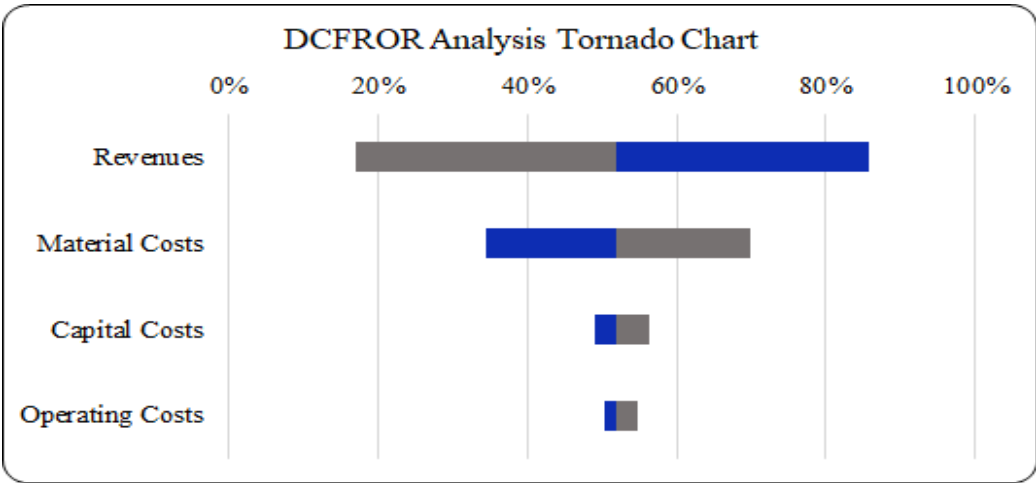
Figures 7 & 8. DCFROR and NPV Sensitivity Analysis for K, Iraq Tax Rate
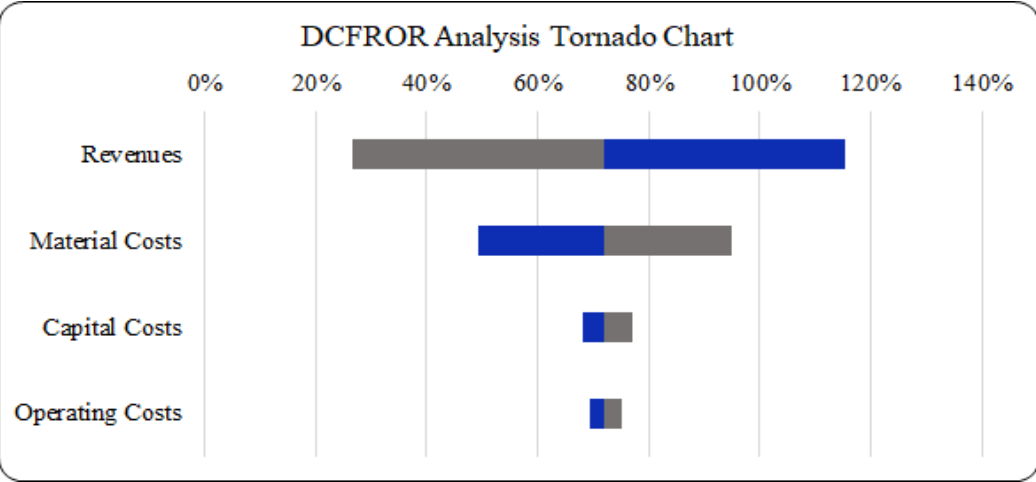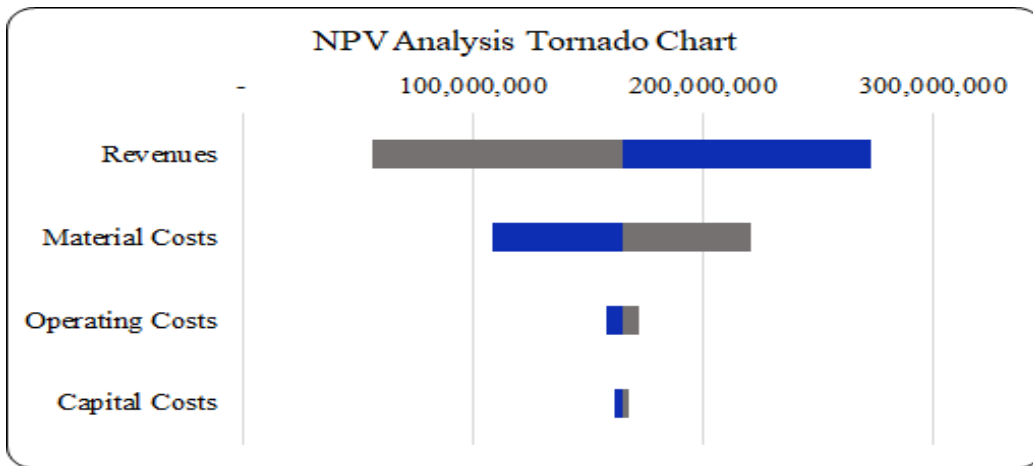
Figures 9 & 10. DCFROR and NPV Sensitivity Analysis for K, Kurdish Tax Rate
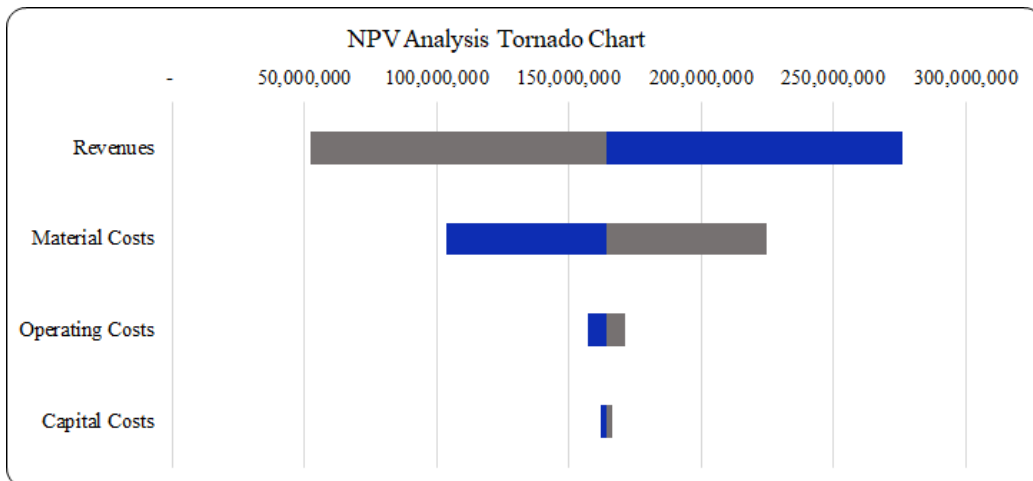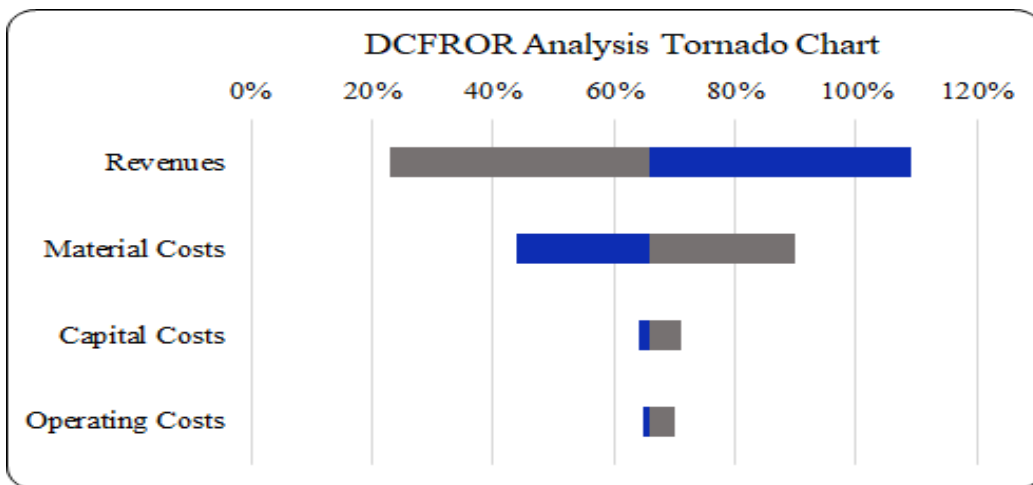
Figures 11 & 12. DCFROR and NPV Sensitivity Analysis for TQ1, Iraq Tax Rate

DCFROR Analysis Tornado Chart

	20%	40%	60%	80%	100%	120%	140%	160%

Revenues

Material Costs

Operating Costs

Capital Costs

NPV Analysis Tornado Chart

	-	100,000,000	200,000,000	300,000,000	400,000,000

Revenues

Material Costs

Operating Costs

Capital Costs
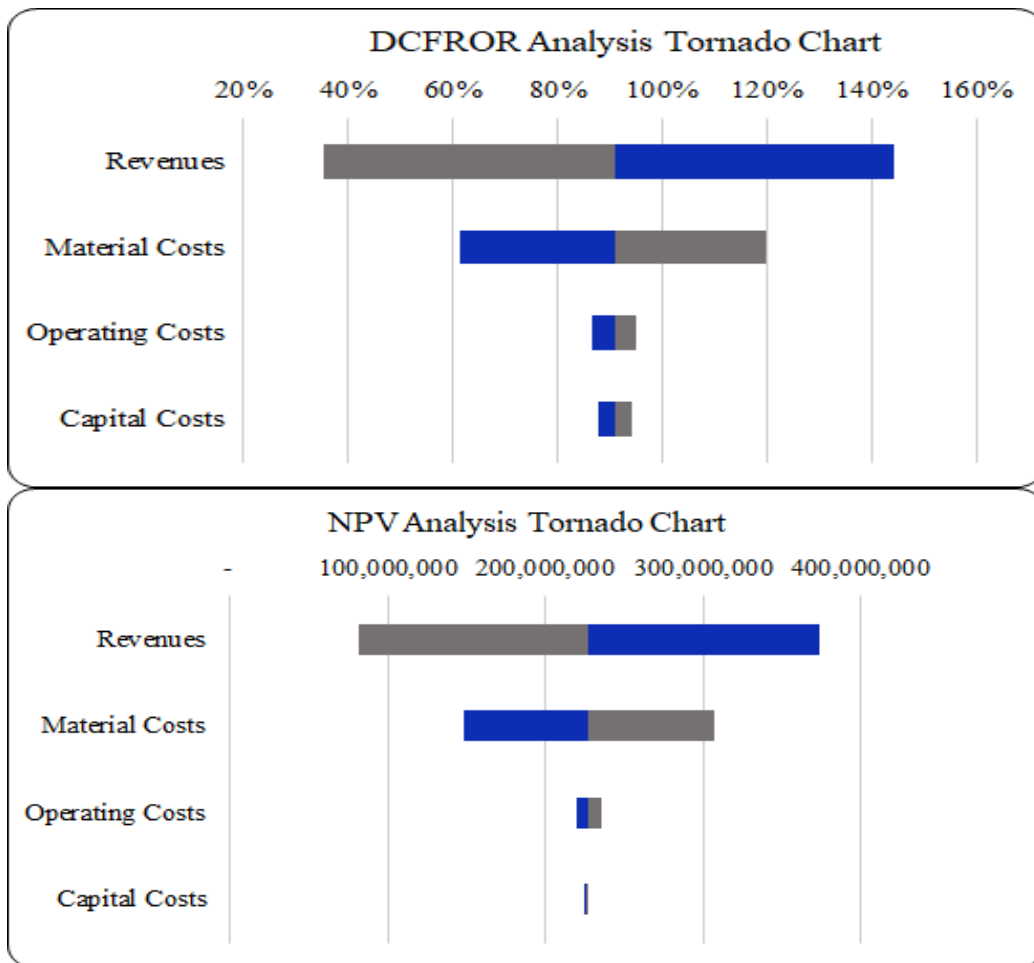
Figures 13 & 14. DCFROR and NPV Sensitivity Analysis for TQ1, Kurdish Tax Rate

Process Safety

Inherent Safety Evaluation

Process safety has many different approaches, but possibly the most effective process safety philosophy is Inherently Safer Design. Inherently safer design focuses on avoiding, eliminating, and reducing hazards in the design phase, as opposed to trying to control hazards. There are four inherently safer design strategies that every project engineer should think about when designing processes: substitution, minimization, moderation, and simplification. The design within this study estimate was created through the lens of inherently safer design and the figure below shows where each strategy can be found (Figure 15).

Inherently Safer Design - Toppings Refinery Retrofit

Substitution
- No major substitutions in chemicals or catalysts were made
- The heating medium before the reactor furnace is substitued with hot process streams via heat integration to reduce furnace size and fuel combustion
- Furnaces used for reboiled absorbers could have been substiuted for a sythetic oil reboiler that could heat to the required temperature

Minimization
- Reaction recycle ratio is at 10% , reducing the amount of chemicals in the reactors
- Sulfolane recycle rate is at 99% so that a smaller inventory of sulfolane is needed for the process. Will require a longer start-up process

Moderation
- Pressures are kept under 10 bar for the entirety of the process (excluding steam)
- High temperatures are needed in the reaction and extraction sections due to reaction kinetics for this process and the high boiling point of sulfolane
- Temperature in the reactors are kept below 535°C to limit side reactions

Simplification
- An extra distillation column is used instead of a steam stripping process before the final distillation section
- The use of multiple furnace passes of the reactor feed is used to control temperature instead of multiple furnaces varying in size
- The heat integration system saves energy but makes the design much more complicated

Figure 15. Inherently Safer Design Applications

Process Safety Management

Process Safety Management (PSM) is a program within chemical processing companies that encompass safety procedures with a goal of identifying, understanding, and controlling process hazards. PSM regulations are general, include OSHA regulations, and the success of a plant's PSM program is measured by the amount of accidents. The base of every PSM system is knowing the hazards associated with the process materials, the process itself, the control systems in place, and the consequences of process upsets. The information below includes a table of pertinent process material information, the suggested P&ID and control system for the major fractionator, the sizing of a relief valve for the major fractionator, a TNT equivalency calculation for if all contents of the major fractionator vent to the atmosphere and deflagrate, the explosivity limits of each of the process components, and a "What-if" Hazards Analysis for the major fractionator.

Process Hazards

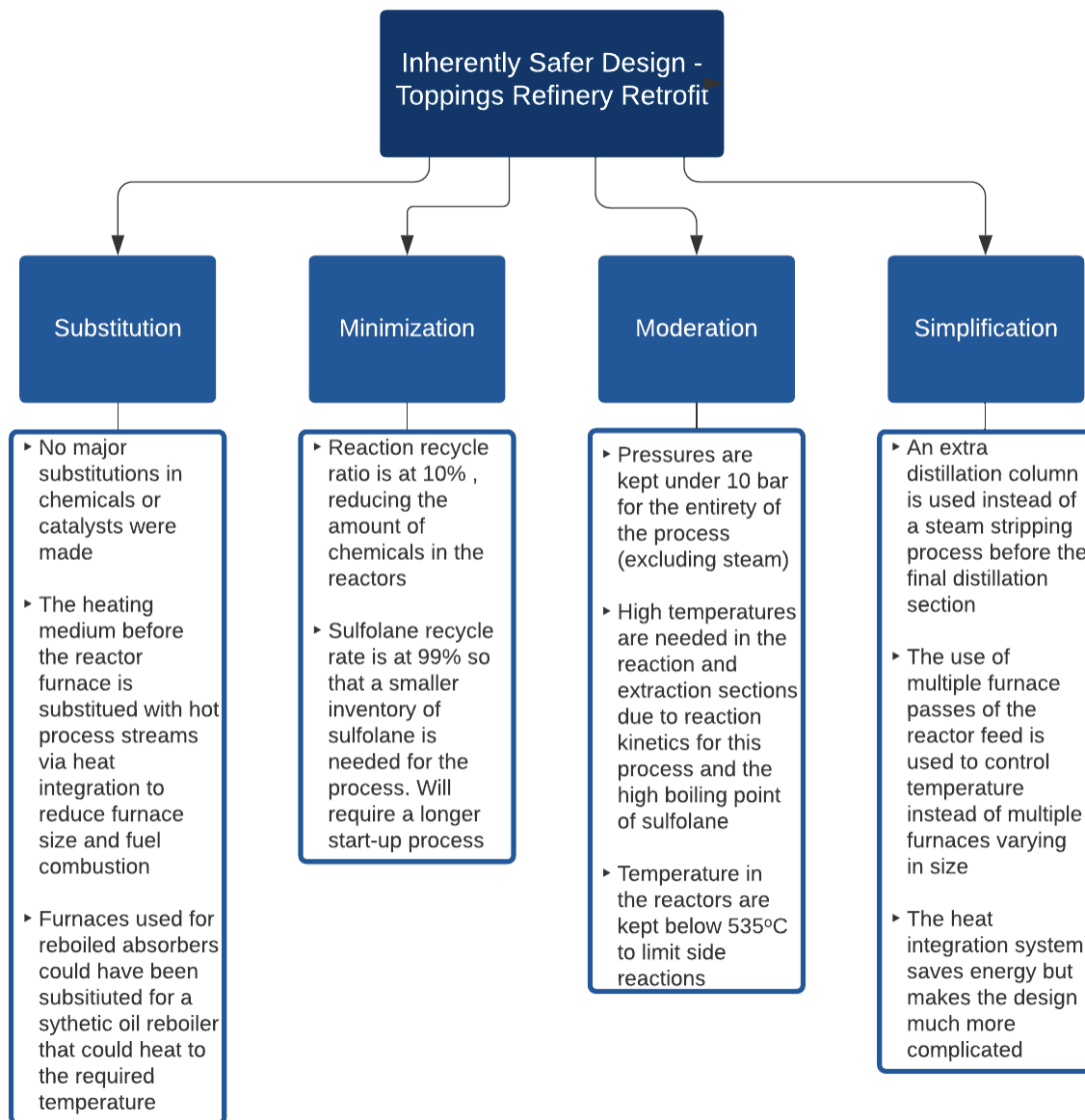Process hazards associated with materials are tabulated below (Table 8). The main hazards resulting from the chemical constituents within the toppings refinery retrofit are flammability concerns. Of the 21 components present throughout the catalytic reforming process that is simulated, fifteen of those have a flammability rating (NFPA) of three or more (out of four). This only raises the importance of keeping the chemicals in the pipes and knowing as soon as a release occurs. Another hazard that is recognized from the table below is the presence of two chemicals that are simple asphyxiants. Special care should be taken when workers are present in areas that could have high concentrations of those species. If small leaks are detected, testing should be conducted to determine if the leak leads to any OSHA violations in terms of permissible exposure limits before repairs are made. The lethal dose limits should not play too much of a factor in safety procedures since the temperatures throughout the process are high. If an event occurs where chemicals are spilled onto a worker more damage will likely occur due to regular burns rather than chemical burns with the chemicals present in this design. In settings where the chemicals are in close proximity with workers such as when samples are taken, care should be taken in handling all chemicals but especially cyclohexane due to its low dermal lethal dose limit.

Table 8. Chemical Hazards Information

	OSHA Chemical Exposure Limits[8]	NFPA diamond Classifications				Lethal dose (LD50) limits (mg/kg)	
	(TWA)	Health	Flammability	Instability	Special	Oral	Dermal
Benzene	10 ppm	2	3	0	0	2000	8260
n-Decane	500 ppm	1	2	0	0	5000	5000
Cyclohexane	300 ppm	2	3	0	0	5000	2000
Toluene	200 ppm	2	3	0	0	5000	12124
Sulfolane	0.37 ppm(not osha)	1	1	0	0	1900	3800
H2O	N/A	0	0	0	0	90000	N/A
p-Xylene	100 ppm	3	3	0	0	5000	N/A
Hydrogen	N/A	0	4	0	0	N/A	N/A
n-Nonane	200 ppm	3	3	0	0	N/A	N/A

n-Octane	500 ppm	3	3	0	0	N/A	N/A
n-Heptane	500ppm	1	3	0	0	5000	3000
n-Hexane	500ppm	2	3	0	0	25000	3000
n-Pentane	1000ppm	1	4	0	0	5000	3000
n-Butane	800 ppm	1	4	0	0	N/A	N/A
Propane	1000 ppm	2	4	0	0	N/A	N/A
Ethane	1000 ppm	1	4	0	0	N/A	N/A
Methane	N/A	1	4	0	0	N/A	N/A
Oxygen	N/A	0	0	0	OX	N/A	N/A
Nitrogen	N/A	0	0	0	SA	N/A	N/A
CO2	5000 ppm	2	0	0	SA	N/A	N/A
CO	50 ppm	3	4	0	0	N/A	N/A

Note: References are not included NFPA Diamond Classifications and LD$_{50}$ values since these were found by finding safety data sheets posted online by various companies and labs

Control System explained

The control system that is shown in the P&ID below was created with the goals of having complete control of pertinent process variables, including several different layers of protection against major process upsets, and giving plant personnel sufficient information to monitor the process. An in-depth explanation of each controller and its respective role is given in Table 9 below.

Table 9. Explanation of Controls System

Controller	Control Variable	Manipulated Variable	Description
AIC 105	Condensed Distillate Temperature	Flow Rate of Cooling Water	Cascade master controller that takes input from the vapor distillate and cooling water lines in the form of flow and temperature measurements and send an ESP to FIC-105
FIC 105	Condensed Distillate Temperature	Flow Rate of Cooling Water	Cascade slave controller that receives the setpoint from AIC-105 and then controls the FCV on the cooling water inlet
PIC 102	Column Pressure	Condensed Distillate Flow into Reflux Drum	Feedback controller that controls pressure of the tower by throttling distillate flow into the reflux drum, allowing controlled flooding, that can make the heat transfer area variable.
TIC101	Distillate Composition	Reflux flow rate into column	Temperature at the top stage of the column is used to infer the composition and the feedback controller will then adjust the reflux ratio to control distillate composition.

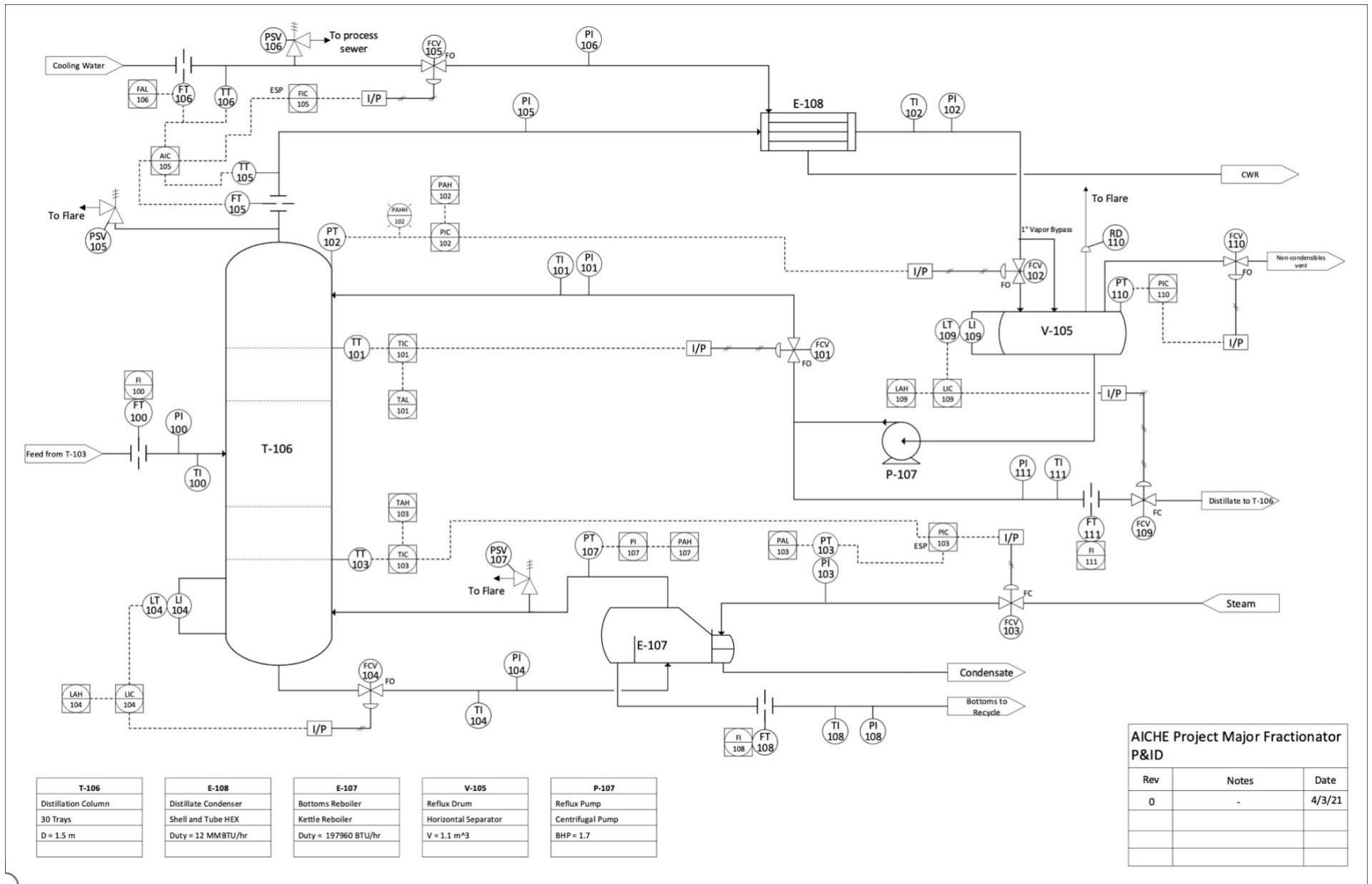| TIC 103	Bottoms Composition	Flow Rate of Steam into Reboiler	Temperature at the bottom stage of the column is used to infer the composition and the master controller will provide an ESP to PIC-103 to control steam inlet flow which in turn affects the boil-up ratio.
PIC 103	Bottoms Composition	Flow Rate of Steam into Reboiler	Cascade slave controller that takes the ESP set by TIC-103, and the pressure of the steam inlet to control the flow of steam to the reboiler.
LIC 104	Liquid holdup level in column	Bottoms flow to Reboiler	Feedback controller that controls the liquid holdup level in column by varying bottoms flow out of the column.
LIC 109	Liquid level in reflux drum	Distillate product flow rate	Feedback controller that controls the liquid level in the reflux drum by controlling distillate flow rate with an FCV.
PIC 110	Pressure in reflux drum	Non-condensable vent flow rate	Feedback controller that controls pressure in the reflux drum by adjusting the FCV of the non-condensable vent.

Relief Valve Sizing

A pressure relief sizing for the major fractionator is conducted with the assumption being that there is an onsite flare available for safe and complete combustion of the vented materials. The first step in this calculation is to determine the overpressure event that requires the highest mass flow rate of relief. This event is determined to be the loss of cooling water. The loss of cooling water leads to no condensation of the vapor distillate, and uncontrollable temperature rising in the column. The equation used to calculate the mass flow rate required for relief for this overpressure event is shown below (Equation 4) with variables for the heat duty of the condenser and the heat of vaporization. Based on the mass flow rate required calculated, and the conditions of the column, such as the lack of corrosive chemicals, the relief device chosen was a pressure relief valve.

$$\dot{m} = \frac{\Delta Q_{relief}}{\lambda} \tag{4}$$

The next step is determining the maximum allowable working pressure (MAWP) of the tower, the maximum overpressure, and then the minimum required area for relief. The MAWP for the column is determined by using a table[10] which states that for vessels where the maximum working pressure is below 50 psig, the MAWP is chosen by adding 10 psi to the maximum working pressure. The set pressure of the relief valve is set to equal the MAWP and the maximum overpressure is then calculated by multiplying the MAWP by 110%. The minimum area required for relief is calculated by using the equation below.

$$A = \frac{\dot{m}}{C_o P\, K_b} \sqrt{\frac{T}{\frac{MW\, \gamma\, g_c}{R} (\frac{2}{\gamma+1})^{(\frac{\gamma+1}{\gamma-1})}}} \tag{5}$$

The variables included in this calculation are as follows: C_o is the orifice coefficient and for this calculation it is assumed to be 0.61, P is the relieving pressure, K_b is the backpressure correction factor and it was determined to be 1 for this scenario using tables from API 520[2] T is the relieving pressure, MW is the molecular weight of the relieving fluid, γ is the ideal gas specific heat ratio, g_c is a conversion factor, and R is the ideal gas constant.

AICHE Project Major Fractionator P&ID

T-106
Distillation Column
30 Trays
D = 1.5 m

E-108
Distillate Condenser
Shell and Tube HEX
Duty = 12 MMBTU/hr

E-107
Bottoms Reboiler
Kettle Reboiler
Duty = 197960 BTU/hr

V-105
Reflux Drum
Horizontal Separator
V = 1.1 m^3

P-107
Reflux Pump
Centrifugal Pump
BHP = 1.7

Rev	Notes	Date
0	-	4/3/21

27

After the area is calculated the orifice designation and valve body can be chosen from the standards of pressure relief valves[2]. The pressure relief valve sizing included for the major fractionator of the toppings refinery retrofit design resulted in an orifice designation of Q and the corresponding valve body size of 6 x 8(in). Table 10 below shows the key values used for this sizing.

Table 10. Pressure Relief Sizing Important Values

Pressure Relief Sizing	
$\Delta Q_{condenser}$ (kj/h)	4890000
λ (kj/kg)	394
$\dot{m}$ (lbm/h)	27350
MAWP (psia)	38
A (in)	9.9
Orifice Designation	Q
Valve Body (in)	6 x 8

Uncongested Vapor Cloud Deflagration

One of the worst-case circumstances for any chemical plant is an uncontrolled release of a large amount of flammable gasses followed by a combustion. This sort of event leads to massive losses in human lives, workdays, and economic value. The chances of such a catastrophic event are small but not zero, therefore considerations should be made to lessen the impact of such an event if it were to occur. One way to lessen the impact is to site offices and control rooms that cannot withstand large blasts a safe distance from possible danger areas. To properly make these considerations one must map the blast radius of the worst-case scenario by using a TNT equivalency calculation of the energy produced from the event. The catastrophic event used in this study estimate is the case of all contents inside of the major fractionator releasing instantaneously as vapor, and then deflagrating.

To complete the TNT equivalency calculation[5], the first step is to calculate the amount of material is contained in the column by component. The simulation program for this design does not include this information forthright, and it must be calculated by using the liquid and vapor densities of each tray and then multiplying them by the volume and component composition. Considerations and estimations are also included for the liquid holdup in the bottom of the distillation column. Once the value of mass of each component is known, those values can be multiplied by their respective heat of combustion value. This then gives the total theoretical energy released for this deflagration. The next step is to calculate the equivalent mass of TNT for the calculation. That calculation is performed by the equation below.

$$m_{TNT} = \frac{\eta \, m \, \Delta H_c}{E_{TNT}} \tag{6}$$

For equation 6, E_{TNT} is the energy produced per kilogram of TNT, η is the empirical explosion efficiency which varies between 1% and 10%, m is the mass of hydrocarbons, and ΔH is the heat of combustion. For the calculation in this estimate, the value of η was chosen to be 5%.

Once m_{TNT} is calculated, the scaled distance is determined from equation 7 at a certain distance from ground zero point of the explosion. Then using z_e, the peak side-on overpressure can be calculated using z_e and atmospheric pressure (equation 8). Then using tables from SOURCE, damage can be estimated at varying distances. The results from this are shown in Table 11.

$$z_e = \frac{r}{m_{TNT}^{1/3}} \tag{7}$$

$$\frac{p_o}{p_a} = \frac{1616[1+(\frac{z_e}{4.5})^2]}{\sqrt{1+(\frac{z_e}{0.048})^2}\sqrt{1+(\frac{z_e}{0.32})^2}\sqrt{1+(\frac{z_e}{1.35})^2}} \tag{8}$$

Table 11. TNT Equivalency Important Values

Uncongested Vapor Cloud Deflagration	
Energy Released by deflagration (kj)	189500
Equivalent mass of TNT (kg)	2020
Safe human distance away from explosion (m)(po=0.3)	1025
lower limit of serious structural damage (m) (po=2.3)	152

Explosivity limits are values that correspond to the concentration range of the component in air, in which they are capable of combustion. The knowledge of these values helps in the calibration of alarms in gas leak detection systems and personal gas monitoring devices. All the values of explosivity limits for the components included in this process are tabulated below (Table 12).

Table 12. Process Chemicals Explosivity Limits

	Explosivity Limits	
	Upper	Lower
Benzene	7.8%	1.2%
n-Decane	5.4%	0.7%
Cyclohexane	8.0%	1.3%
Toluene	7.1%	1.1%
SULFOLANE	N/A	N/A
H2O	N/A	N/A
p-Xylene	7.0%	0.9%
Hydrogen	75.0%	4.0%
n-Nonane	2.9%	0.8%
n-Octane	6.5%	1.0%

n-Heptane	6.7%	1.0%
n-Hexane	7.5%	1.1%
n-Pentane	7.8%	1.5%
n-Butane	8.5%	1.9%
Propane	9.5%	2.1%
Ethane	12.5%	3.0%
Methane	15.0%	5.0%
Oxygen	N/A	N/A
Nitrogen	N/A	N/A
CO2	N/A	N/A
CO	74.0%	12.5%

The "What-if" Hazard analysis below (Table 13), includes a range of events that could occur and cause a process upset in some way or another. Many of the lines of defenses included are a part of the P&ID covered earlier.

Table 13. "What-if" Hazard Analysis

Hazard/Hazardous Event and Mechanism	Consequence	Lines of Defense	Hazard Rating/ Risk Analysis Acceptance of Risk	Recommendations or Action Plan
Loss of cooling water	-Overpressure of V-105 -Process Upset	-Level and Pressure Indicators on V-105 -FAL on CW -Non-condensable vent and rupture drum on V-105	Frequency: High Consequences: Low Class 1	-Prepare shut-down plan for this case
Loss of steam	-Process upset	-PAL on steam line	Frequency: High Consequences: Low Class 1	-Prepare shut-down plan for this case
Vessel failure of column	-Release of flammable liquids/vapors	- Design Pressure of vessel -Operating within limits	Frequency: Very Low Consequences: Severe	- Set in place evacuation plan and raise awareness about what alarm sounds like -Pressure tests

	-Possible vapor cloud deflagration	-PSV to relieve overpressure situations -PAH and PAHH to warn of overpressure event	Class 1	
Reboiler tube rupture	-E-107 Overpressure -Column overpressure -Process Upset -Possible leakage of process fluid into condensate line	-PSV on boil-up line -PSV on column -PAH on boil-up line	Frequency: High Consequences: Low Class 1	- Prepare shut-down plan for this case and try to contain water from contaminating column contents
Reflux pump failure	-Process upset -Possible V-105 flooding	-Spare pump	Frequency: Low Consequences: Low Class 1	- Scheduled pump maintenance
Failure of pneumatic system	-Process upset -Light components in bottom product	-Fail safe positions on control valves set up to prevent overpressure event	Frequency: Low Consequences: Moderate Class 1	- No recommendations
Level Indicator Failure on Tower	-Possible flooding of boil up line -Overpressure	-PSV on tower to prevent overpressure -PAH on column	Frequency: Low Consequences: Moderate Class 1	-Frequent LT calibrations
Level Indicator Failure on reflux drum	-Condenser flooding that causes loss of duty -Overpressure of V-105 -Flooding of non-condensable vent -Loss of liquid seal in V-105 then possible	-Rupture disk on V-100 -Non-condensable vent line with pressure controller	Frequency: Low Consequences: Moderate Class 1	-Frequent LT calibrations

	vapor in reflux pump			

Safety Summary

Safety is the number one priority in every plant, but extra efforts must be taken within plants where a strong safety culture is not established yet. To ensure the small toppings refinery that Mr. Abbasi is running does not get shut down by the Iraqi government, who is cracking down on small refineries that have insufficient safety, operational standards, and efficiency; it is strongly suggested that all safety recommendations be seriously considered. Producing a design that is inherently safe is nearly impossible, but every process can be designed to be inherently safer. For the sake of safety, all possible process hazards should be eliminated, mitigated, identified, monitored, or controlled, and this is the basis for the strategies involved with PSM and inherently safer design. For the design in question, the main hazards arise from the large amounts of flammable materials being processed. The main safety recommendations that stem from this hazard include the flame resistant personal protective equipment (PPE), gas leak detection devices located around the plant, personal gas detection devices available for when work involves a possible ignition source, and proper alarm systems for dangerous conditions that employees are aware of.

Although this design was created with the principles of inherently safer design in mind and many choices reflect the strategies within that system, there are some areas in which the strategies were not adhered to. The complexity of the heat integration system, the high temperatures required for the reaction section, and the use of fired heaters for reboilers are the main violators of the inherently safer design strategies. The reaction section temperatures are unavoidable at this point in the understanding of catalytic reforming, and the heat integration will save money in the form of energy usage, so the complexity has been deemed an acceptable trade-off. If a hot synthetic oil system were available, it could be used and would reduce hazards in the plant.

It is recommended that other areas of the process continue to follow the Best Available Control Technology (BACT) strategy in the design of the P&IDs, so that operators have the capability to monitor and have complete control of the process. Discoveries from the "What-if" Hazard Analysis lead to the recommendations of creating shutdown plans for the case of loss of cooling/heating, evacuation plans for vessel failure of distillation columns, scheduled pump maintenance, and level transmitter calibrations. All of which should be included in the standard operating procedures for the plant. Lastly, it is recommended that the siting of office and other non-blast proof buildings should be at least 152 m away from the distillation section, and any workers within 1,025 m should wear PPE of at least a hard hat and shatterproof safety glasses.

Conclusions

The results from the study estimate of the Toppings Refinery Retrofit in Kirkuk, Iraq exhibit a project that is economically and technically feasible, while also limiting safety risk to an acceptable amount. The goal of this unit is to produce light hydrocarbon, gasoline, benzene, toluene, and para-xylene product streams from the light sweet crudes exiting other sections of Mr. Abbasi's refinery.

Values determined from an economic analysis of the project with the Iraqi tax rate and feed conditions of K indicate that it has a high probability of producing substantial profits. This addition to the small toppings refinery will produce an NPV of $113.3 million, using an approximate yearly sales revenue of $191.1 million, operating costs of $11.5 million, a fixed capital investment of $64.1 million, and working capital costs (deriving from the cost of catalyst and sulfolane used for extraction) of $9.6 million. This equates to a DCFROR of 47% and a discounted payback period of 2.59 years. The

condition of Iraqi tax and feed K result in the least economically attractive outcome; other possibilities such as Kurdish tax and feed conditions of TQ1 generate an expected DCFROR of 91%. Conclusions from a sensitivity analysis of the project determine that the only conditions that would result in a DCFROR lower than 15%, the minimum rate of return used for the project, are if the revenues deviate negatively by approximately 20%. This is for the case of Iraqi tax and feed K results as well.

The design of the process can be split up into three major sections: the reactor section, extraction section, and the distillation section. Within the reactor section, the temperatures were controlled by using two instances of heat integration, and multiple tube passes within a furnace to optimize the reaction kinetics. Heat from the fully reacted process stream and sulfolane exiting a reboiled absorber within the extraction section were utilized within the heat integration system. 10% of the light hydrocarbon purge is recycled back into the reactors to supply the reactors with more hydrogen. The extraction section consists of two liquid-liquid extractors and two reboiled absorbers. Due to the high boiling point of sulfolane, fired heaters are required for both reboiled absorbers. The necessity of furnaces instead of reboilers reduces the efficiency of the section and it is recommended that a synthetic hot oil utility should be researched for this process to reduce hazards and increase efficiency. To increase the efficiencies in the distillation section and make the distillations easier to produce a BTX product with 99% purity an extra distillation column was added in comparison to the base case process (SOURCE).

All economic results and key design decisions are meaningless if the design produced has unacceptable risk associated with it. In order to ensure acceptable risk, the plant needs to have a strong safety culture where safety is valued just as much as production, and the plant should be designed through the philosophy of inherently safer design. The main process hazards associated with the toppings refinery retrofit are associated with the large amounts of highly flammable process materials. Per the results from a TNT equivalency calculation of the deflagration of the major fractionator contents, it is recommended that buildings are sited 152 meters away from the major fractionator and workers within 1,025 meters must wear flame resistant clothing, hard hats, and shatterproof safety glasses as PPE. Using the explosivity limits given in this study estimate, it is recommended that a gas leak detection system be installed. Lastly, standard operating procedures should be created to ensure proper maintenance of control system instrumentation and operating limits are set and followed.

Appendix

Reactor Train Detail

Introduction

The reaction section consists principally of three packed bed reactors, PBR-101, PBR-102 and PBR-103 (now referred to in aggregate as the reactor train). The reactor train is the most critical set of equipment in the unit concerning both function and cost. All downstream processes' functions are contingent upon naphtha being suitably converted, and, due to the high cost of platinum metal, the active catalyst, the packed bed reactors are by far the costliest pieces of equipment in the unit. In the event of reactor train under-performance, shutdown, or failure, the effects will be felt throughout the entirety of the process and run the risk of producing low quality products or creating unsafe conditions. For this reason, the project team includes in this appendix a detailed description of methods used to simulate reactor performance, a description of maintenance concerns and strategies, and a detailed summary of principles promoting design conditions, and reactor performance metrics.

Supplementary pieces of equipment dedicated to the function of the reactors are also among the costliest in the process, and certainly among the most critical. The feed pump P-101, pre-heating equipment E-101, E-102, and FH-101, and recycle compressor K-101, are principal among them, while

V-101 and T-101 are needed to remove non-salable components from the reactor train outlet in to produce the extraction section feed.

Due to the complexities of naphtha compositions, all simulations use proxies in the determination of reactor performance, consequently, the reactor train is also the greatest source of error in design estimations. More detailed studies will be required to precisely determine necessary capital and utility costs, but calculations from these proxies are deemed appropriate for a preliminary study.

The reactor train is simulated using Aspen HYSYS

Reaction Summary

Constituent Reactions

In simulation of reactor performance, four reactions are assumed to occur simultaneously when feed reactants are in contact with platinum catalyst.

Reaction 1 is the dehydrogenation of cycloalkanes and polyaromatic hydrocarbons to produce aromatics. This reaction is deemed desirable, as it eliminates undesirable cycloalkanes and polyaromatic hydrocarbons and produces usable hydrogen gas and salable aromatics. However, it should be noted that this reaction is highly endothermic and imposes an associated operating cost with reheating the reactor feed following its occurrence. Cyclohexane is used as a proxy component to represent all cycloalkanes and polyaromatic hydrocarbons, and Benzene is used as a proxy component to represent all aromatics.

Reaction 2 is the hydrogenation (cracking) of low-octane linear alkanes to produce high octane linear alkanes and other lower-value hydrocarbons. This reaction is deemed desirable, as it eliminates undesirable linear alkanes to produce salable high-octane linear alkanes. This reaction is also exothermic, heating the feed and reducing operating costs associated with reheating the reactor feed following its occurrence. n-Decane is used as a proxy component to represent all low-octane linear-alkanes.

Reaction 3 is the cracking of cycloalkanes and polyaromatic hydrocarbons to produce lower-value hydrocarbons. This reaction is deemed undesirable, as it consumes cycloalkanes and polyaromatic hydrocarbons, which could otherwise contribute to Reaction 1, and hydrogen, which could otherwise contribute to Reaction 2, to produce non-salable, low value hydrocarbons. While this reaction is exothermic, can reduce operating costs associated with feed heating, and does eliminate undesirable compounds, it is otherwise detrimental to the process and its profitability. Cyclohexane is used as a proxy component to represent all cycloalkanes and polyaromatics.

Reaction 4 is the cyclization of linear alkanes into cycloalkanes. This reaction is deemed acceptable, as it produces hydrogen which can be used in Reaction 2 and cycloalkanes which can be used in Reaction 1, as well as being exothermic and reducing operating costs associated with heating. However, it consumes salable linear alkanes, subsequently reducing gasoline production, and produces cycloalkanes which, if not consumed by Reaction 1 or Reaction 3, run the risk of compromising fuel quality. Cyclohexane is used as a proxy component for cycloalkanes. The reactants, products, and value to the process of the reactions are summarized in Table 14.

Table 14. Reaction Summary

Reaction Summary			
Reaction	**Reactants**	**Products**	**Value**
Reaction 1	C_6H_{12}	C_6H_6 H_2	Desirable

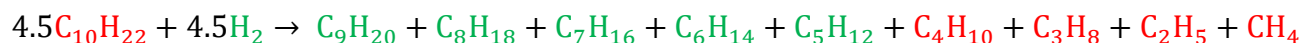|			
Reaction 2	$C_{10}H_{22}$ H_2	C_1-C_9	Desirable
Reaction 3	C_6H_{12} H_2	C_1-C_5	Undesirable
Reaction 4	C_6H_{14}	C_6H_{12} H_2	Neutral

Stoichiometry

Stoichiometric equations for each of these reactions, using proxy components, are provided below, with desirable compounds highlighted in green and undesirable compounds highlighted in red.

Reaction 1

$$C_6H_{12} \leftrightharpoons C_6H_6 + 3H_2$$

Reaction 2

$$4.5C_{10}H_{22} + 4.5H_2 \rightarrow C_9H_{20} + C_8H_{18} + C_7H_{16} + C_6H_{14} + C_5H_{12} + C_4H_{10} + C_3H_8 + C_2H_5 + CH_4$$

Reaction 3

$$5C_6H_{12} + 10H_2 \rightarrow 2C_5H_{12} + 2C_4H_{10} + 2C_3H_8 + 2C_2H_5 + 2CH_4$$

Reaction 4

$$C_6H_{14} \leftrightharpoons C_6H_{12} + H_2$$

Note that Reaction 1, Reaction 3, and Reaction 4, have a molar excess, Reaction 1, and Reaction 4 are reversible, and Reaction 1 is endothermic with all other reactions being exothermic. These properties are summarized in Table 15.

Table 15. Reaction Stoichiometry

Reaction Stoichiometry			
Reaction	**Molar Excess?**	**Reversible?**	**ΔH**
Reaction 1	Yes	Yes	Endothermic
Reaction 2	No	No	Exothermic
Reaction 3	Yes	No	Exothermic
Reaction 4	Yes	Yes	Exothermic

Kinetics

Kinetic Equations for each reaction, using proxy components, are provided below.

Reaction 1

$$r = 9.4928 \times 10^{13} e^{\frac{-150606.4}{8.314T}} P_{C_6H_{12}} - 8.2728 \times 10^{-4} e^{\frac{52170.4}{8.314T}} P_{C_6H_6} P_{H_2}^3$$

Reaction 2

$$r = 3.6704 \times 10^{21} e^{\frac{-287756.8}{8.314T}} P_{C_{10}H_{22}}$$

Reaction 3

$$r = 3.6704 \times 10^{21} e^{\frac{-287756.8}{8.314T}} P_{C_6H_{12}}$$

Reaction 4

$$r = 4.19816 \times 10^{21} e^{\frac{-312237.9}{8.314T}} P_{C_6H_{14}} - 3.33674 \times 10^{19} e^{\frac{-275285.8}{8.314T}} P_{C_6H_{12}} P_{H_2}$$

$$r \equiv \frac{kmol}{m^3 hr} \qquad\qquad P \equiv MPa \qquad\qquad T \equiv K$$

Where r is the rate of reaction, T is temperature, and P_i is the partial pressure of component i. Kinetic parameters are tabulated in Table 16.

Table 16. Kinetic Parameters

Kinetic Parameters				
$Ae^{-\frac{E}{RT}} \prod_i R_i^{n_i} - A'e^{-\frac{E'}{RT}} \prod_i P_i^{n_i}$				
Reaction	$A\,[\frac{kmol}{m^3 - hr - MPa}]$	$A'[\frac{kmol}{m^3 - hr - MPa}]$	$E\,[\frac{kJ}{mol}]$	$E'[\frac{kJ}{mol}]$
Reaction 1	9.5×10^{13}	8.3×10^{-4}	150.6	-52.2
Reaction 2	3.7×10^{21}	NA	287.8	NA
Reaction 3	3.7×10^{21}	NA	287.8	NA
Reaction 4	4.2×10^{21}	3.3×10^{19}	312.2	275.3

Immediate consequences of these kinetic parameters are that, for a given set of concentrations, the selectivity towards Reaction 1 increases with decreasing temperatures, and vice versa, Reaction 4 is only a major contributor at elevated temperatures, and increases in the partial pressure of hydrogen severely reduce, and even reverse, the rate of Reaction 1. These considerations are discussed in more detail in the Operating Conditions section.

Catalyst Details

The reactor train uses powdered platinum metal on alumina support as catalyst, with an aluminum composition of 0.6 wt. % platinum. Platinum, being a precious metal, requires high capital investment to be obtained, but can be used continuously for extended periods, provided that the catalyst is regenerated when performance is found to no longer be acceptable, mainly due to coke deposits collecting on the catalyst. This is discussed in more detail in the maintenance section. The alumina supports under consideration are half inch diameter spheres. Relevant physical properties used for simulation and determination of catalyst masses are tabulated in Table 17.

Table 17. Catalyst Physical Properties

Catalyst Physical Properties	
Alumina Density (kg/m³)	3800

|	
Specific Heat Capacity of Alumina (kJ/kg-C)	0.88
Void Fraction	0.5
Weight Percent Platinum	0.6

## Operating Conditions

Pressures and Temperatures

Reactor train conditions are chosen to prevent operation under extreme conditions when possible and are otherwise chosen to bias reaction selectivities towards desirable reactions.

The reactor feed is pumped to 700kPa before entering the pre-heating stage. A feed pressure of 700kPa is chosen to minimize risks associated with operating subsequent vessels at extreme pressures, as well as bias reaction selectivity towards Reaction 1. Pressure drops across reactors are relatively low, approximately 45kPa across the whole reactor train, due to the reactors' sizes and the relatively large diameter of the catalyst supports. This allows the entirety of the reactor train to operate under pressures that select for favorable reactions, while preempting the potential for increased pressure drops over time due to coke deposits.

The reactor feed is pre-heated three times before being fed to the first reactor PBR-101, at 478°C. A relatively low temperature is chosen for PBR-101 both to limit the temperatures of subsequent units and to utilize the high selectivity of Reaction 1 at this temperature to reduce the contribution of Reaction 3 in subsequent units. The feed enters PBR 103 at 526°C. Temperatures are elevated in this reactor to promote Reaction 3 and Reaction 4. The feed then enters PBR-102 at 498°C. Temperatures are lowered compared to PBR-103 to improve selectivity for newly formed cycloalkanes towards dehydrogenation while maintaining a high enough temperature for cracking reactions to continue.

Illustrations of the effects of temperature and pressure on reaction extents for feed K are given below in Figure 17 & 18.
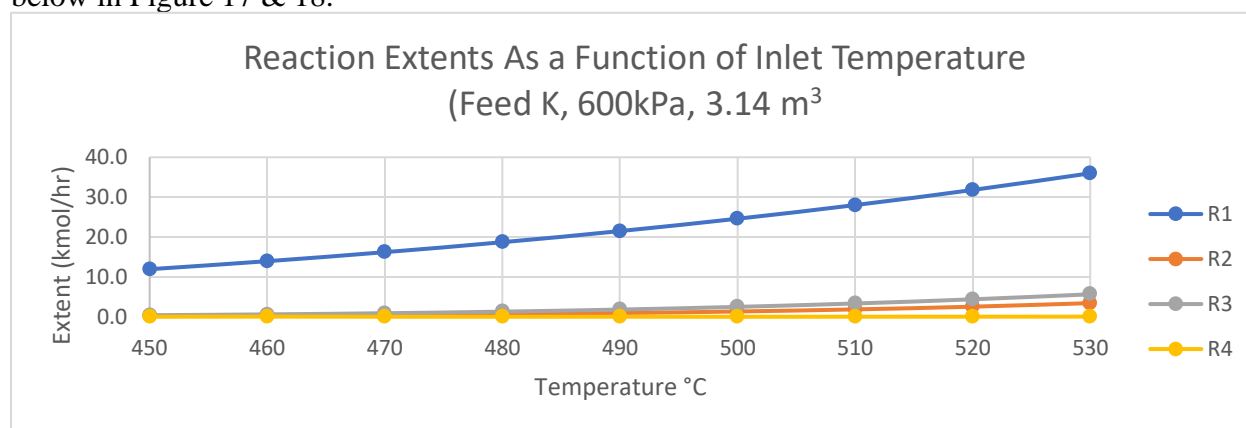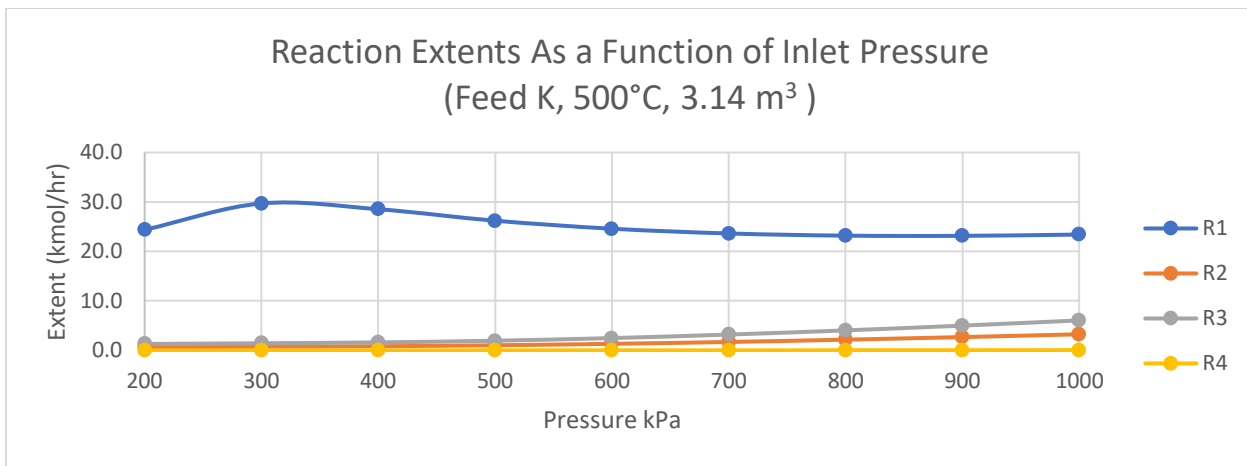
Figures 17 & 18. Reaction Extents as a Function of Inlet Temperature and Pressure

Light Gas Recycle

A fraction of product non-condensables are recycled to combine with feed naphthas to form the reactor train feed, with the goal of reducing coking of the catalyst bed and increasing the time that the reactors can be active before requiring regeneration. Secondarily, hydrogen content ensures that cracking reactions can continue throughout the reactors' operation.

Due to the utility costs associated with heating and cooling additional material, pressure losses associated with additional material flowing through the reactor train, and adverse effects on reaction kinetics due to the addition of inert components, this design opts for a relatively low recycle rate of 10% of non-condensables to the reactor train feed. To compensate for the low rate of recycle, large reactors are utilized to limit the buildup of coke on catalysts by allowing feed to flow through a larger volume.

Equipment Sizing and Configuration

Reactors are sized with the intent to limit coke build-up and the time between regeneration cycles, with PBR-102 being the largest reactor with respect to diameter, length, and total volume. The inlet of PBR-101 is heated three times before entry to limit the size of any individual heater, and the outlet of PBR-101 is heated once before being fed to PBR-103. The outlet of PBR-103 is not heated further, both because it is not required for functional operation and opting not to do so reduces the heat duty of the fired heater FH-101, and the duty of the reactor train product cooler. PBR-102 and PBR-103, while not utilizing interstage cooling, are still kept as two separate pieces of equipment both to reduce the size of any individual reactor, and to reduce the size required of a spare reactor during maintenance.

Due to the small recycle rate, the compressor required to deliver recycle to the reactor feed, K-101, requires low power, and is consequently relatively small, the same is true of its knockout drum V-102.

E-103, V-101, and T-101 which produce the extraction section feed from the reactor train outlet are among the largest pieces of equipment in the process and are consequently of considerable size.

Major Vessel properties are summarized in Table 18.

Table 18. Equipment Properties

Vessels/Towers	R-101	R-102	R-103	T-101	V-101
Temperature (°C)	479	527	498	99	35
Pressure (kPa)	920	892	881	198	795.3

Orientation	Horizontal	Horizontal	Horizontal	Vertical	Vertical
MOC	CS	CS	CS	CS	CS
Size					
Height/Length (m)	8	8	8.5	6.9	1.9
Diameter (m)	1.25	1.75	2.125	1.5	0.9
Internals	Platinum on alumina	Platinum on alumina	Platinum on alumina	sieve	N/A

Maintenance

Catalyst Regeneration

Due to the gradual deactivation of catalyst, catalyst regeneration is an eventuality that the project team uses as a guiding principle to determine reactor size, number, and configuration. While regeneration is occurring, whatever reactor is undergoing regeneration cannot be used as a reaction vessel by the process.

Reactor sizes are larger than would otherwise be required to achieve adequate conversion in anticipation of a reduction in catalyst activity during periods between regeneration. Additionally, reactor temperatures do not exceed 535°C as a precaution to avoid increased coke deposits associated with operating at higher temperatures.

To mitigate losses associated with maintenance down time, the project team elects to use a swing reactor to allow continuous operation during regeneration cycles, discussed in more detail below.

When catalyst regeneration is required, the reactor to be regenerated is routed over by the process. The catalyst to be regenerated is put in contact with flaming vapors to burn coke deposits built up on catalysts. This process carries a risk of unexpected reactions, considering that the distribution of coke is not uniform, and should be undertaken with care to promote safe operation.

Spare (Swing) Reactor

When catalyst regeneration is required, a "swing" reactor is employed to allow operation to continue when regeneration is required, or to replace an underperforming unit with a higher performing unit to be regenerated later. This enables flexibility in operation at all times and eliminates the need for complete shutdown when regeneration is required.

The swing reactor is sized identically to PBR-102, the largest reactor in the reactor train, so it may replace any reactor in the train without a loss in overall reactor volume. This also allows the swing reactor to be used for extended periods of time if catalyst regeneration cannot be performed immediately. However, only one reactor can be down at any one time, as the design does not permit the replacement of two reactors with one.

Performance Metrics

Reaction Extents and Conversions

Individual reaction extents are used as a metric of performance, as well as overall extent and conversion of the reactor train for each reaction. It should be noted that the majority of reaction activity takes place in **PBR-102** and **PBR-103**, while **PBR-101** is used to selectively perform Reaction 1. Individual reactor extents, and overall reactor train extents, are tabulated in Table 19.

Table 19. Individual Reactor Extents

Reaction	PBR-101 Extent (kmol/hr)	PBR-102 Extent (kmol/hr)	PBR-103 Extent (kmol/hr)	Overall Extent (kmol/hr)
Reaction 1	20.1	6.4	48.6	75.1
Reacton 2	1.5	13.6	23.6	38.8
Reaction 3	2.9	1.4	17.2	21.5
Reaction 4	0.0	4.4	0.3	4.7

Reaction Selectivities

The project team uses as an alternative metric of performance each reactor's, and the reactor train as a whole's, selectivity towards reactions deemed desirable over reactions deemed undesirable (see Table m+1). This is a critical metric concerning reactions that consume valuable components, or that consume components that would be more valuable being used as reactants in other reactions.

Cycloalkane dehydrogenation, is used as the reference reaction for these selectivities, that is to say, the selectivity of Reaction 1, over Reaction 1, is 1, the selectivity of Reaction 1 over Reaction 2 is the ratio of the extent of Reaction 1 to Reaction 2, etc. Ideally, the selectivity over Reaction 3 should always be large, and the selectivity over Reaction 2 should be large compared to the selectivity over Reaction 3. The selectivity for individual reactors, and the reactor train, are tabulated in Table 20.

Table 20. Individual Reactor Selectivities

Selectivity	PBR-101	PBR-102	PBR-103	Overall
Selectivity 1/2	13.4	0.5	2.1	16.0
Selectivity 1/3	7.1	4.5	2.8	3.5
Selectivity 1/4	-1259.5	1.5	162.9	16.1

Equipment Expenses

Capital Costs

Capital costs associated with the reactor train are substantial. The reactor train, and particularly the required catalysts, are the greatest capital cost incurred among all process equipment. Also of particular note is FH-101. An itemization of bare module costs for feed K is given in Table 21.

Table 21. Bare Modulus Costs for Reactor Section

Equipment	Bare Module Cost

PBR-101 (Packed)	$6,149,000
PBR-103 (Packed)	$12,041,000
PBR-102 (Packed)	$18,843,000
Swing Reactor	$18,430,000
FH101	$236,000
K-101	$184,000
V-101	$145,000
V-102	$74,000
T-101	$107,000
E-101	$258,000
E-102	$273,000
E-103	$691,000
E-104	$304,000
P-101	$63,000
Total	$57,798,000

Operating Costs

Operating costs associated with the reactor train are substantial. Due to the temperatures required by component reactions, large utilities are associated with heating and subsequent cooling of feed and recycle streams, with Fired Heater FH-101 and HE-103 being of particular note.

As detailed in the economic analysis, the number of operators needed per shift is estimated to be 4. Labor costs are approximated based on the decision that one of these 4 operators be assigned to operation of the Reactor Train during all shifts. Subsequently the labor cost for the section is determined as one fourth of the labor cost for the plant. An itemization of operating costs for the Reactor Train for feed K is given in Table 22.

Table 22. Operating Costs for the Reaction Section

Total Utility Costs	$3,778,000
Labor Cost	$68,000
Total Operating Costs	$3,845,000

Extractor Section Detail

Prior to entering the extraction section of the plant, the product stream from the reactor train is processed by two separator vessels. These columns increase the concentration of benzene and separate light carbon chains from the valuable benzene-laden flow. An important assumption that is made at this

stage of the process is that when referring to benzene and in all technical modeling that was produced, benzene is representative of all aromatics. Making this assumption allows for the use of robust software to simulate sections of the plant with relative ease compared to every possible reaction product being produced. The benzene will eventually include toluene and paraxylene, taken into consideration in the distillation section. The benzene stream from the reaction stream feeds into heat exchanger E-106 at a rate of 26,000 kilograms per hour, of which over 7400 kilogram per hour is benzene. After utilizing the heat exchanger with cooling water to cool the benzene stream, liquid extractor T-102 passes the benzene-laden stream across a solvent stream composed of greater than 99.9% sulfolane on a mass basis. Sulfolane then extracts over 99.9% of the benzene that enters the extraction section. Trace amounts of carbon components also pass into the solvent in this vessel, composing 1.5% of flow to the larger 7.3% benzene composition. The majority of light carbon components exit the extractor without being retained in the solvent. At this point, benzene has effectively been stripped of light residuals that will be processed for sale as gasoline and diesel fuel. The light carbons are passed through another liquid extractor, T-103, with pure water. This tower extracts any sulfolane retained by the light stream allowing sulfolane retention by the system to be recycled and used again in the first extractor. The water stream from the extractors is then processed in reboiled absorber T-105, recovering sulfolane from water and producing steam. The T-105 recovery process saves 34 kilograms of sulfolane every hour and is recombined with the main sulfolane stream exiting T-104.

The main sulfolane stream, now carrying benzene, exits T-102 to enter absorption column T-104. T-104 removes 99.8% of the desired benzene product from the solvent. The extraction process is now completed with regard to extracting benzene from a flow of mixed carbon chains. The benzene stream carrying 8600 kilogram per hour of benzene will exit the extraction section of the process and will next enter the major fractionator, T-106, in the distillation section. Equipment summary table 23 shows the installed cost of each piece of equipment.

Table 23: Installed Cost for Extraction Section Equipment

Equipment	Bare Module Cost	Equipment	Bare Module Cost
P-104	$25,000	FH-102	$3,630,000
P-105	$15,000	FH-103	$199,000
P-106	$11,000	T-102	$96,000
V-103	$726,000	T-103	$62,000
V-104	$117,000	T-104	$183,000
E-105	$120,000	T-105	$72,000
E-106	$143,000	Total Equipment Cost	$5,399,000
		Total Operating Cost	$8,368,000

The bottoms product of T-104 contains the majority of sulfolane that is fed to the first liquid extractor. During the study estimate, the large cost of sulfolane became a point of concern when designing an economically feasible process. Instead of using sulfolane once-through and buying more or buying some make up amount, the solvent should be recycled and reused. Sulfolane should be infrequently purchased in large quantities and contained fully within the extraction section of the plant.

With the lump-sum purchase of enough solvent to operate the system on a 5-year time schedule. Eventually, sulfolane should be replaced in its entirety. This method of purchasing also allows for high flow of solvent through the process, maintaining the efficacy of the extraction process when alternate feeds are used in the plant. Not only will reuse of the solvent save money, the sulfolane stream will leave T-104 above 300°C, with a mass flow rate of 138,000 kilogram per hour. The study estimate dictates this stream be 35°C when entering the first extractor. This acts as an opportunity for heat integration to save money in place of paying for cooling water. An additional cost comparison can be done to justify the use of T-103. The second liquid-liquid extractor is responsible for saving approximately 34 kg/hr of sulfolane from leaving the system with desired fuel streams. This tower is also responsible for production of the bulk of salable gasoline and diesel fuel streams after recovering any retained sulfolane. The total cost associated with T-103 and the water feed pump are under $100,000, including a spare pump and drives. The cost of continually purchasing sulfolane to make up the amount lost without the extractor is equivalent to $1.4 million each year in make up. The value of sulfolane incentivizes recovery on its own, but T-103 is producing the majority of salable gas streams, separating $40 million of diesel fuel and $74.5 million of gasoline to sell each year. Once solvent streams pass through towers, they recombine to be used to preheat feed K in the reaction section of the plant. After cooling takes place, the large solvent stream mixes with the cooled benzene stream from E-106 before entering the first liquid extractor, T-102.

The operating costs of the extraction section include costs of water used for sulfolane retention, cooling water utilities to ensure efficacy of sulfolane as a solvent, electricity to drive pumps between process vessels, the costs associated with reboiling processes attached to absorbers and distillation fractionators and the operation costs of staffing personnel to safely tend to equipment of this plant section. The service costs associated with the extraction section of the plant are calculated at $72,000 on a yearly basis. This figure is based on the number of vessels and equipment within the extraction section that need shift operators. The $72,000 per year also accounts for service costs and maintenance fees that are expected to accompany the extraction units. Routine cleaning of process equipment is good practice to increase the longevity of operating equipment and ensures that operation of the equipment will continue to yield efficacy near modeled results for the duration of the project life. The operating cost for the extraction section is stated in Table 23.

Temperature profiles of distillation fractionators in the extraction area are presented below. Graphs have been given for both reboiled absorption towers that were used for component recovery and separation. The heating duty for both towers at the respective operating pressures required large reboiler duty, reaching temperatures greater than 300°C. The following figures show the required temperature for each of the reboiled absorbers.
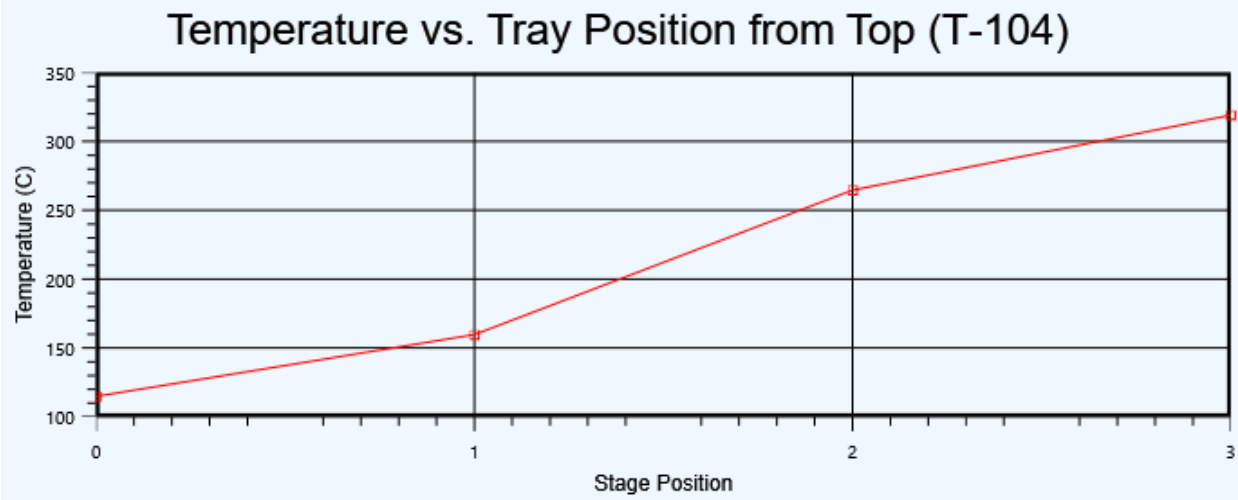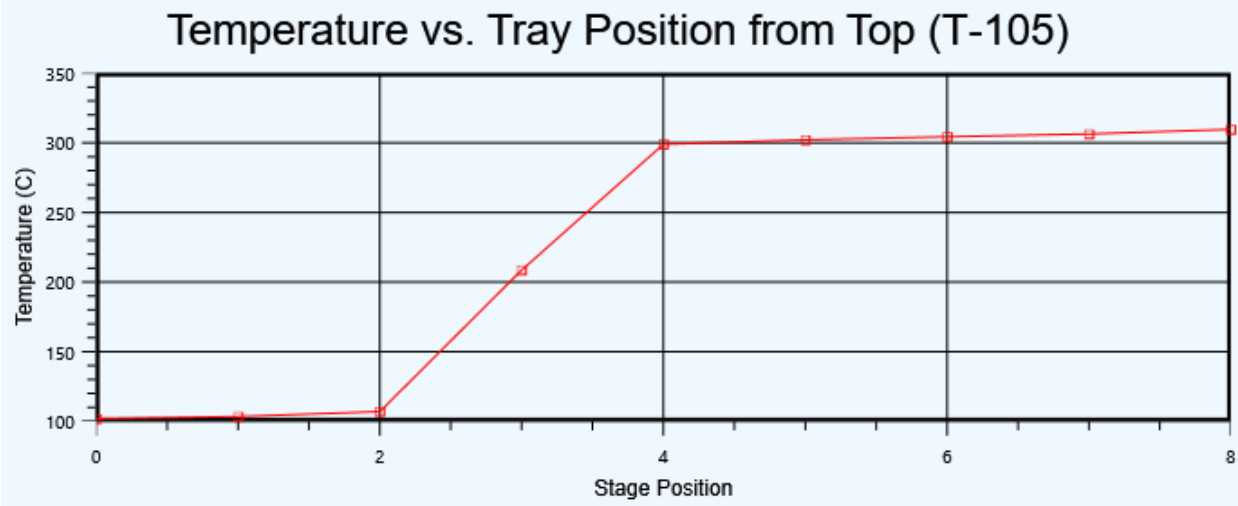
Figure 19: Temperature Profile of T-104

Figure 20: Temperature Profile of T-105

Typical reboilers operate with the use of steam heating, passing steam at high temperature and pressure through tubes that contact the bottoms flow from tower units. The heating requirements for both absorbers ruled out the possibility of using a high-pressure steam utility stream. The maximum temperature of high-pressure steam the plant has access to is 240°C. This requirement led to opportunities for innovation. Kettle reboilers for the extraction section are instead planned to be fired heaters. The option of using kettle reboilers or some other heat exchanger model with hot synthetic oil to replace high pressure steam was another consideration. Fired heaters are already being used on the site, so material to operate additional, smaller heaters is readily available. Use of fired heaters also negates the risk associated with additional chemical components and the cost associated with acquiring synthetic oil.

Distillation Section Detail

The distillation section consists of 4 distillation towers. The first tower (T-106) separates the heavy hydrocarbons from the BTX (benzene, toluene, and para-xylene), followed by the second tower (T-107) taking the vapor from T-106 and separating the BTX from the light hydrocarbons. T-108 takes the bottoms from T-107 and separates benzene from the toluene and para-xylene. Lastly T-109 separates

the liquid toluene and para-xylene. The base process flow diagram provided by AIChE only accounts for 3 total distillation columns. The first would separate all hydrocarbons from the BTX stream, followed by the separation of the BTX in the next 2 columns. For this project it is beneficial to have 2 columns for the hydrocarbon separation from BTX due to the amount of heavy hydrocarbons that come out of the extraction section. Having 1 column results in purity of BTX < 99%. Towers are sized by assuming an efficiency of 70% for each tower and then calculating the required tray number by taking the value from the simulation and dividing it by the efficiency. Diameter is calculated using Fair's Method and tray spacing is determined from Wankat[14]. Volume is then calculated using the required tray numbers and values calculated as seen in Table 24. T-106 is the largest distillation column as expected due to the amount of material being separated compared to the latter columns. Tray requirement is also an important factor looked at when comparing volumes as the BTX separation columns require only 29 trays while the columns removing hydrocarbons require more trays to achieve the desired goal of 99% benzene.

Table 24. Distillation Sizing Values

Equipment	Required Trays	Diameter (m)	Tray Spacing (m)	Volume (m^3)
T-106	43	4.86	0.30	24.47
T-107	43	2.98	0.30	8.45
T-108	29	1.85	0.46	2.82
T-109	29	1.15	0.51	.77

Relative volatilities of components being separated in T-108 and T-109 are located in Table 28. As seen in Table 25 the relative volatilities for each component are larger in higher stages of the tower. The separation becomes less difficult as the compound is heated through the tower. When comparing values across towers it is clear that the separation of benzene from toluene and para-xylene is less difficult than the separation between toluene and para-xylene. Benzene having a relative volatility with toluene of 2.749 and 6.985 with para-xylene, shows that the benzene will be easily separated while toluene and para-xylene only reach 2.339 in T-109.

Table 25. Relative Component Volatilities in T-108 and T-109

T-108		T-109	
Stage	**Benzene - Toluene Volatility**	**Stage**	**Toluene - Para-Xylene Volatility**
1	2.749	1	2.339
30	2.130	20	1.899
Stage	**Benzene - Para-Xylene Volatility**		
1	6.985		
30	4.466		

Table 26. Bare Modulus and Operating Costs for Distillation Section in Feed K

Equipment	Bare Module Cost	Equipment	Bare Module Cost
T-106	$ 225,000	E-118	$ 732,000
T-107	$ 190,000	E-119	$ 90,000
T-108	$ 100,000	P-107	$ 34,000
T-109	$ 68,000	P-108	$ 51,000
E-108	$ 691,000	P-109	$ 32,000
E-109	$ 180,000	P-110	$ 24,000
E-110	$ 157,000	P-111	$ 36,000
E-111	$ 330,000	P-112	$ 20,000
E-112	$ 137,000	P-113	$ 31,000
E-113	$ 214,000	P-114	$ 23,000
E-114	$ 203,000	V-105	$ 31,000
E-115	$ 139,000	V-106	$ 23,000
E-116	$ 164,000	V-107	$ 15,000
E-117	$ 176,000	V-108	$ 25,000
Total Utility Cost	$ 1,808,000	**Total Labor Cost**	$ 135,000

The bare modulus cost and utility costs are broken down in Table 26. Bare modulus cost is calculated by taking the purchase cost and multiplying it by the bare modulus factor, pressure factor, and material factor. The highest costing piece of equipment is E-117 which is the reboiler attached to distillation column T-109. This column is responsible for separating toluene and para-xylene is determined by the relative volatilities to be the hardest separation between T-108 and T-109. Utility costs are calculated for each section based on the consumption of the respective utility. Labor costs are calculated using equation 1. Due to the method used for calculating operators per shift, the number of operators will be split between the plant by the number of equipment in each section. The distillation section has 16 of the 36 total units used to calculate labor costs. With 4 operators per shift as calculated by total number of equipment, the distillation section will consume half of the labor costs as it will have 2 operators working on the section.

Temperature profiles are provided in the figures below. T-106 and T-107 have similar profiles as expected due to them both separating BTX from hydrocarbons. In Figure 21 the temperature at stage 15 rises due to the feed stream coming into the column at this stage. Vapor coming up from the reboiler is being cooled by the reflux from the condensing unit. Benzene composition increases from stage 15 to 30 while the heavy hydrocarbons have a sudden decrease in composition moving down the column from

stage 1 due to the temperature change. Figure 22 shows a similar trend in T-107 in which as soon as temperature increases going into stage 1 the light hydrocarbon compositions immediately decrease with a sharp increase in benzene compositions. The following figures (23 and 24) share similar temperature profiles. T-108 and T-109 have a more linear temperature profile, with a major difference in overall temperature within the columns. T-108 has a lower temperature at stage 1 to allow for the separation of benzene and toluene initially and at stage 10 the toluene composition will peak, and the separation of benzene and para-xylene begins. At stage 15 the feed is entering the column and both toluene and para-xylene compositions will increase to stage 30 with the rise in temperature. T-109 is simpler as only toluene and para-xylene are separating. However, a higher temperature is required to allow for this separation to occur as seen in Figure 24. Toluene composition will decrease moving towards stage 20 while para-xylene composition will increase.
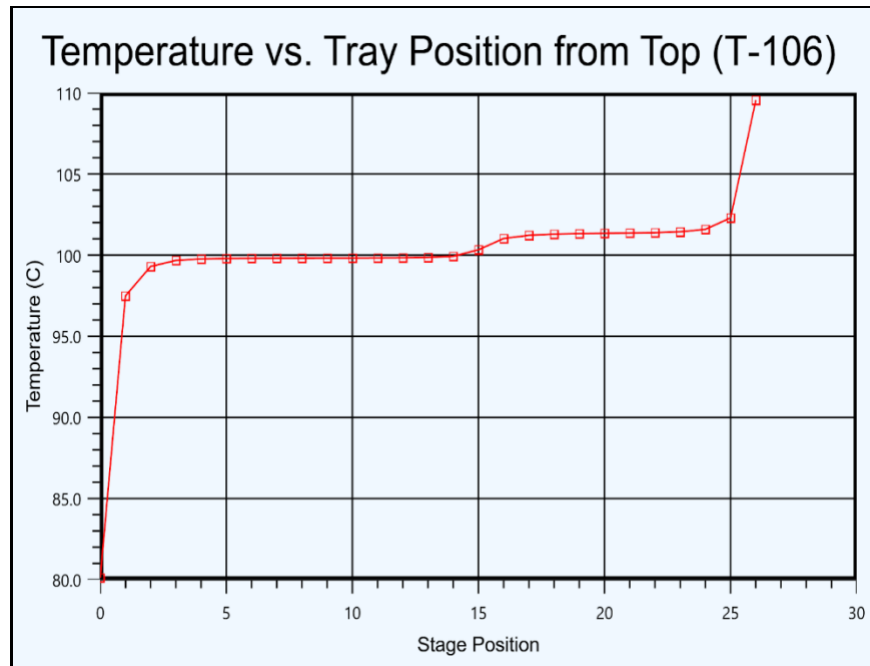

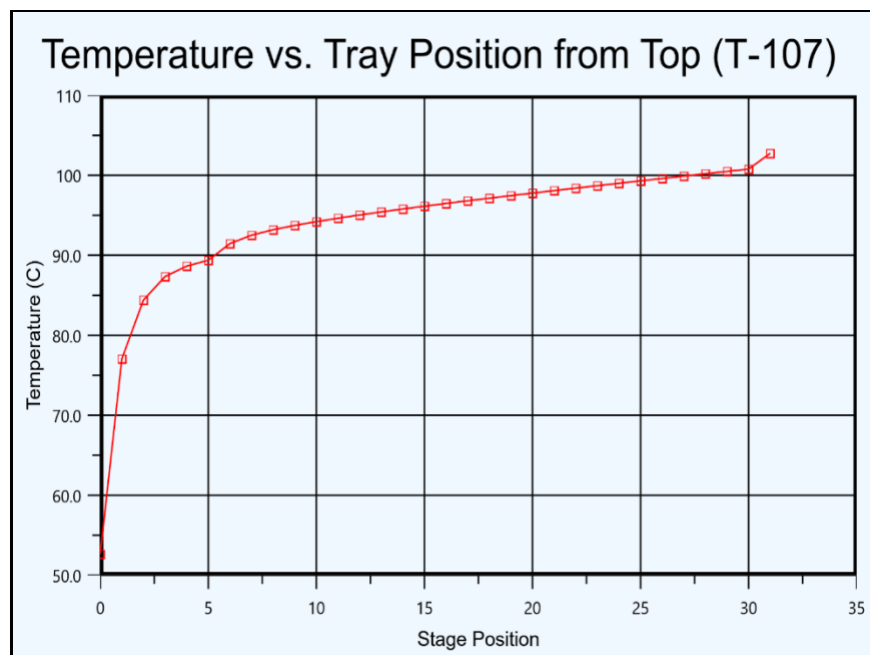Figure 21. Temperature Profile of T-106
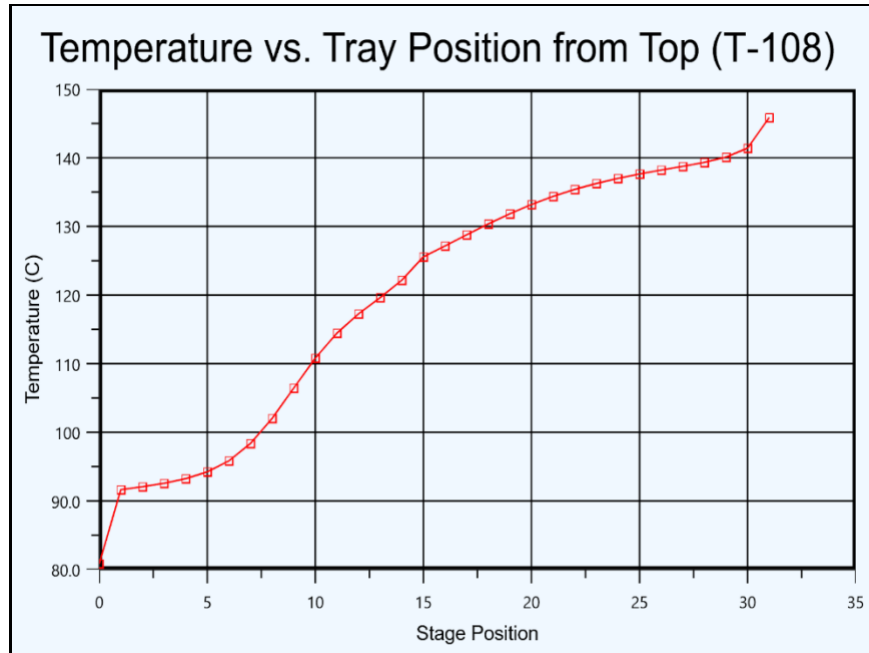
Figure 22. Temperature Profile of T-107
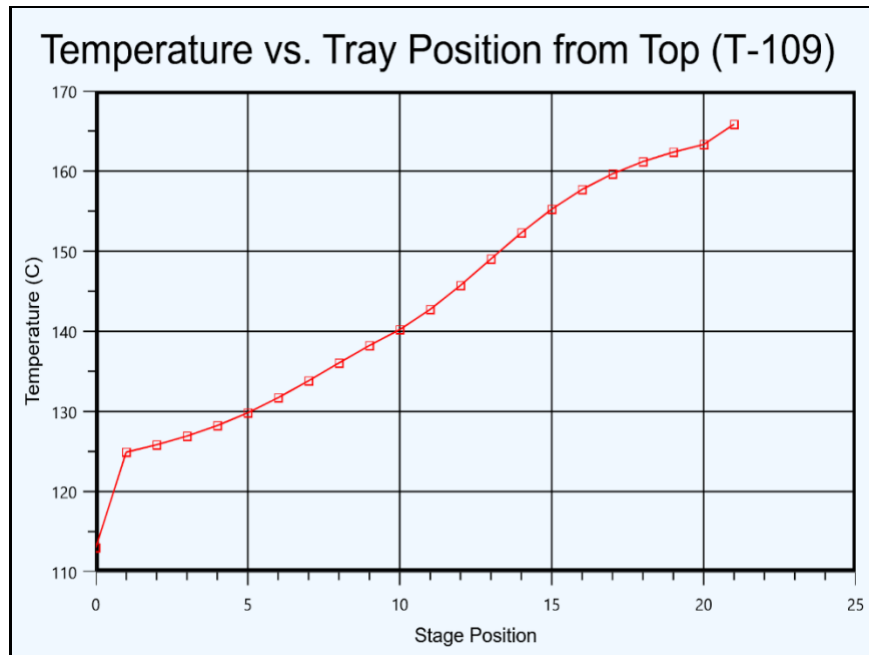

Figure 23. Temperature Profile of T-108

Figure 24. Temperature Profile of T-109

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