Synthesis of Toluene via Propane Dehydrocyclodimerization

Volume 1

Presented by Group 15

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Executive Summary

This report presents the process synthesis and design of a high-volume toluene production plant. This plant was designed to accommodate for a total production capacity of 100,000 metric tons for benzene, toluene and xylenes (BTX). The design follows the Cyclar process, which uses liquefied petroleum gases as a feedstock along with a H-ZSM5 zeolite catalyst in order to produce aromatic hydrocarbons, namely toluene, benzene and xylenes. This synthesis pathway is quite complex, consisting of 79 reactions and 19 compounds, which have very different reaction rates. Process simulations were performed using UniSim.

It was determined that for a BTX yearly production rate of 100,000 metric tons, a total of 202,100 metric tons of raw material would be required, per year. The raw material is available as 95% propane and 5% butane. The BTX produced required a purity of at least 95%, in order to be sold as petroleum grade aromatic hydrocarbons. The benzene, toluene and xylene purities obtained were 96.9%, 98.9% and 98.0%, respectively.

The total grass root cost of the plant was estimated at $45.6M, with corresponding yearly manufacturing costs of $244M. The revenues from the resale of BTX were estimated at $72.6M per year. Following a thorough economic and profitability analysis for a ten-year project life, it was concluded that the net present value was of -$697M. Therefore, it was determined that this plant would not be built, unless process modifications were to be made and the oil market would be more appealing.

Table of Contents

CHAPTER 1: BACKGROUND INFORMATION

CHAPTER 2: PROCESS DESCRIPTION

CHAPTER 6: ENVIRONMENTAL AND SAFETY CONSIDERATIONS

CHAPTER 7: CAPITAL ESTIMATE

CHAPTER 11: CONCLUSION AND RECOMMENDATIONS

List of Figures

List of Tables

Nomenclature

Equipment Labels

FH	Fired Heaters
HX	Heat Exchangers
P	Pump
R	Reactor
RG	Regenerator
T	Tower
VL	Valve
V	Vessel

Chapters 1 to 6

Abbreviations

ACM	Activity Coefficient Model
BTX	Benzene, Toluene and Xylenes
CCR	Continuous Catalyst Regeneration
EOS	Equation of State
Ga-ZSM5	Gallium-doped ZSM5 catalyst
LPG	Liquefied Petroleum Gas
ODE	Ordinary Differential Equations
PBR	Packed Bed Reactor
PR	Peng-Robinson
PFD	Process Flow Diagram
H-ZSM5	Protonated ZSM5 catalyst
SRK	Soave-Redlich-Kwong

Symbols

E_a	Activation Energy (J/mol)
C_j	Cost of Species j (USD)
G	Gibbs Free Energy (J/mol)
$\dot{m}_J$	Mass Flowrate of Species j (kg/h)
P_m	Partial Pressure of Species m (Pa)
A_0	Pre-exponential Factor (mol/kg catalyst h Pa or mol/kg catalyst h Pa^2)
P	Pressure (Pa)
k_j	Rate Constant of Reaction j (mol/kg catalyst h Pa or mol/kg catalyst h Pa^2)
r_j	Reaction Rate of Reaction j (mol/m^3)
T	Temperature (K or °C)
R	Universal Gas Constant (J/mol K)

Chapters 7 to 9

Abbreviations

BV	Book Value
CF	Cash Flow
CCF	Cumulative Cash Flow
CCP	Cumulative Cash Flow Position
CCR	Cumulative Cash Ratio
NPV	Cumulative Discounted Cash Position
DCF	Discounted Cash Flow
DCFROR	Discounted Cash Flow Rate of Return
DCCF	Discounted Cumulative Cash Flow
DCCP	Discounted Cumulative Cash Position
DPBP	Discounted Payback Period
FCI/FCI_L	Fixed Capital Investment with/without Land
COM/COM_d	Manufacturing Cost with/without Depreciation
PBP	Payback Period
PVR	Present Value Ratio
ROROI	Rate of Return on Investment
S	Salvage Value
SF	Stream Factor
WC	Working Capital

Symbols

S	Allowable Stress (bar)
C_{BM}	Bare Module Cost ($)
F_{BM}	Bare Module Factor
B_i	Bare Module Factor Constants
A	Capacity of Equipment
CA	Corrosion Allowance (m)
C_{RM}	Cost of Raw Materials ($)
C_{UT}	Cost of Utilities ($)
C_{WT}	Cost of Waste Treatment ($)
d_k^{DDB}	Depreciation (Double Declining Method) ($)
D	Diameter of Vessel (m)
C_{GR}	Grass Root Cost ($)
F_M	Material Factor
N_{OL}	Number of Operators per Shift
N_{np}	Number of Processing Steps (including non-particulate solids)
C_{OL}	Operating Labour Costs ($)
F_p	Pressure Factor
C_i	Pressure Factor Constants
P	Pressure of Equipment (barg)
P	Number of Processing Step (including particulate solids)

C_p	Purchase Cost (\$)
K_i	Purchase Cost constants
C_{TM}	Total Module Cost (\$)
t	Vessel Thickness (m)
E	Welding Efficiency

CHAPTER 1
BACKGROUND INFORMATION
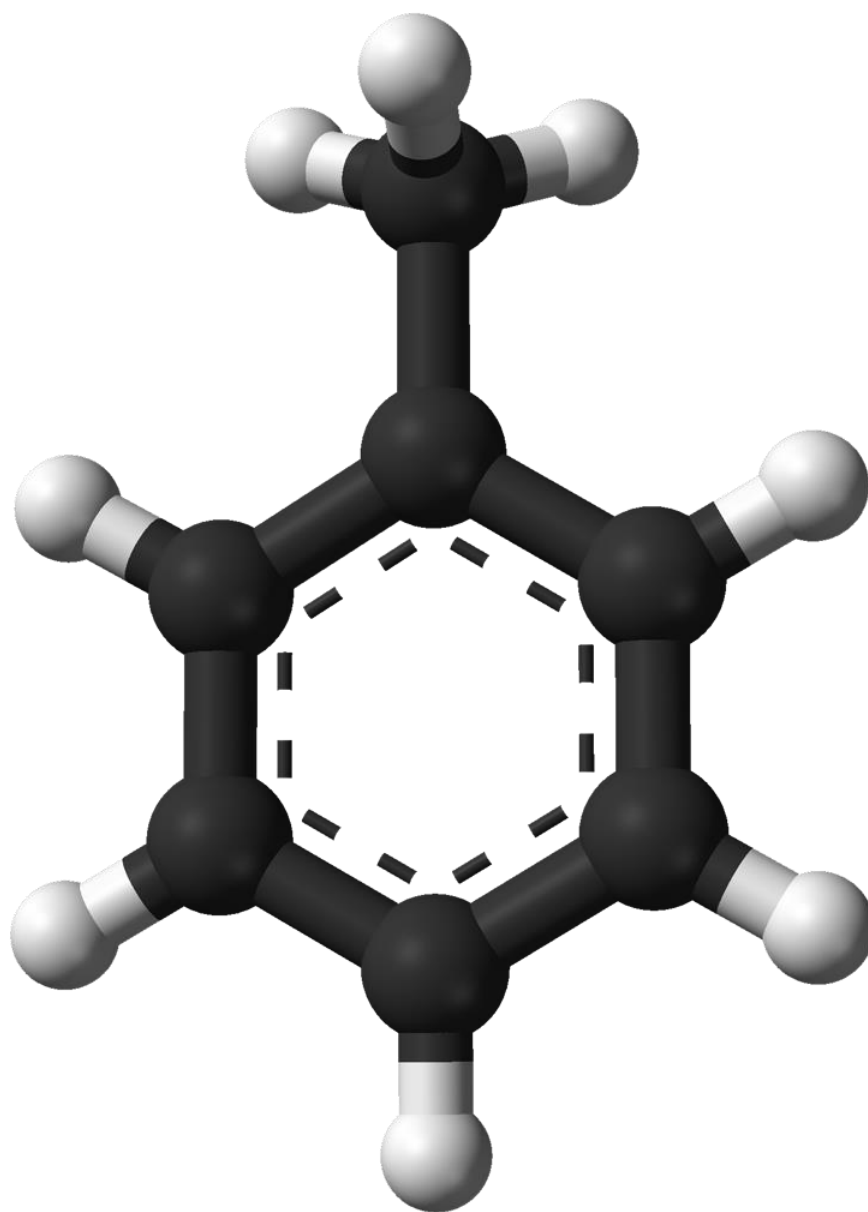
1.1 Historical Background

Toluene is an aromatic hydrocarbon. It naturally occurs in crude oil as well as in tolu balsam, a resin found mainly in South America [1]. Prior to World War I, toluene was mainly recovered from coke oven. When the war started in 1914, an increasing demand in toluene arose for the production of trinitrotoluene (TNT). In order to meet the production demands, toluene was also recovered from petroleum sources for the first time. The manufacture of toluene from petroleum sources increased significantly during World War II for use in aviation fuel [2]. In 1940, the Baytown Ordonance Works (BOW) became the world's first commercial synthetic toluene plant and was built for the U.S. War Department. The plant quickly exceeded its production capacity of 2,200 barrels per day. Most of the toluene manufactured was used to produce TNT and as an aviation fuel additive to improve octane ratings. In total, the facility produced approximately 5.5 million barrels of toluene, most of which were used to produce two thirds of the TNT used by the U.S. military in World War II [3].

1.2 Common Applications

The primary use for toluene is the production of benzene (50%). It is also used in gasoline blending, along with benzene and xylene, to increase octane ratings (34%). Many compounds are derived from toluene, including toluene diisocyanate (9%), solvents (5%) and other chemicals (2%) [4].

Some of the commercial applications of toluene include the manufacture of paint and paint thinners, nail polish, adhesives, rubber, nylon and plastics, and it is also used in some printing and leather tanning processes [1]. Toluene is present in various household products where it makes up 12% of their composition on average [5]. Moreover, toluene was used as an anti-parasitic medicinal agent to treat roundworms and hookworms [4].

Toluene can be produced in three different grades, depending on the intended use for the product. The TDI Grade is mostly used for the production of consumer goods such as isocyanates. The Nitration Grade is present in the solvent market, as well as in the manufacture of benzene and phenol. Finally, the Commercial Grade is used to make benzene, but most of it is returned to the gasoline pool in order to obtain higher-octane fuel products [6]. Toluene has two main advantages of being used as a blending agent in gasoline fuels. First, its low volatility,

caused by the methyl group, allows it to blend with gasoline mixtures comprised of less expensive materials having higher volatilities (i.e. n-butane). And secondly, toluene has a higher octane number than premium and unleaded gasoline [2].

Storing hydrogen safely has been an important issue limiting the implementation of hydrogen vehicles [7]. The usage of toluene has been proposed as a solution to this issue because it is a good hydrogen carrier that can be dehydrogenated and hydrogenated readily in presence of an appropriate catalyst [7]. It is too soon to say whether this strategy will be implemented in the future, but toluene certainly appears to be a promising candidate for this application.

1.3   Current Industries and Marketplace Perspective

The total manufacturing capacity for toluene production plants across the United States was 5.33 million tonnes in 1989. It was produced by 21 companies at 30 different locations. Eight of these facilities had annual capacities exceeding 0.18 million tonnes, accounting for 72% of the toluene capacity in the United States. These facilities were Amoco, Exxon, BP, Sun, Amerada Hess, Phillips, Mobil and Chevron [4]. Most of the toluene was manufactured from naphtha reforming. In fact, 99.5% of the toluene was derived from petroleum fractions: 94.5% was produced using catalytic reformate, 5% from pyrolysis gasoline, and 0.5% from coke-oven light oil [4].

In 1994, the global production of toluene was estimated at 10 million tonnes, from which more than 3 million tonnes were manufactured in the United States [5]. The consumption of toluene in North America and Western Europe decreased by 8% and 17%, respectively, amidst the economic recession of 2008-2009. Contrarily, the Middle East, Northeast and Southeast Asia showed a slight increase in production during the same time frame. Since 2010, the toluene production and demand rates have increased. As the global economies recover, the toluene market should improve [8]. Figure 1 is a pie chart representing the world consumption ratios of toluene in 2012.

World Consumption of Toluene—2012
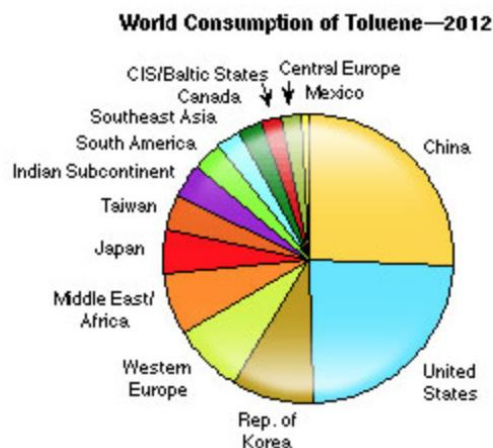
Figure 1 – Global toluene consumption distribution in 2012 [8]

Estimates suggest that continued investments in developing countries will increase the demand of toluene derivatives by 5.2% each year, with growth rates over 10% anticipated in China, India and Taiwan. Northeast Asia had the largest toluene demand market rate in 2012, at just over 46%. In 2012, it was estimated that the global toluene demand market grew by 5.3% [8].

Figure 2 represents the global toluene production capacity in 2014 [9].

Global Toluene Capacity by Region (2014)
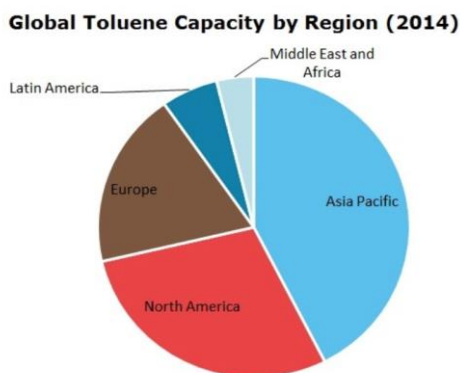
Figure 2 – Global toluene production capacity distribution in 2014 [9]

As illustrated in Figure 2, Asia Pacific is the region that has the largest production and demand rate worldwide. China and the United States consume approximately 50% of the total toluene produced [9].

Now is a good time to increase the toluene production rate because the global demand is rapidly increasing. From 2000 to 2010 the global demand for toluene increased from 10,380,023 to

12,441,568 tons. The majority of the increased demand originated from the Asia Pacific region. Forecast estimates expect that the Asia Pacific region will account for 51.4% of the global toluene demand by 2020, where the global demand is expected to have increased to 19,603,561 tons [10].

1.4 Possible Plant Location

Following a global market analysis, possible plant locations were determined for the synthesis of toluene. The three best options are Asia Pacific, Saudi Arabia, as well as North America. The main factors considered in this analysis were the availability and cost of the raw material as well as the proximity to target markets. It was found in literature that Asia Pacific imports most of its LPG resources from Saudi Arabia, and therefore constructing the plant in this location would not be economically beneficial, even though there is a high demand rate. There are large quantities of LPG readily available in Saudi Arabia, however, their cost is higher than in the United States, as shown in Figure 3, and there is a limited market for toluene in the Middle East.
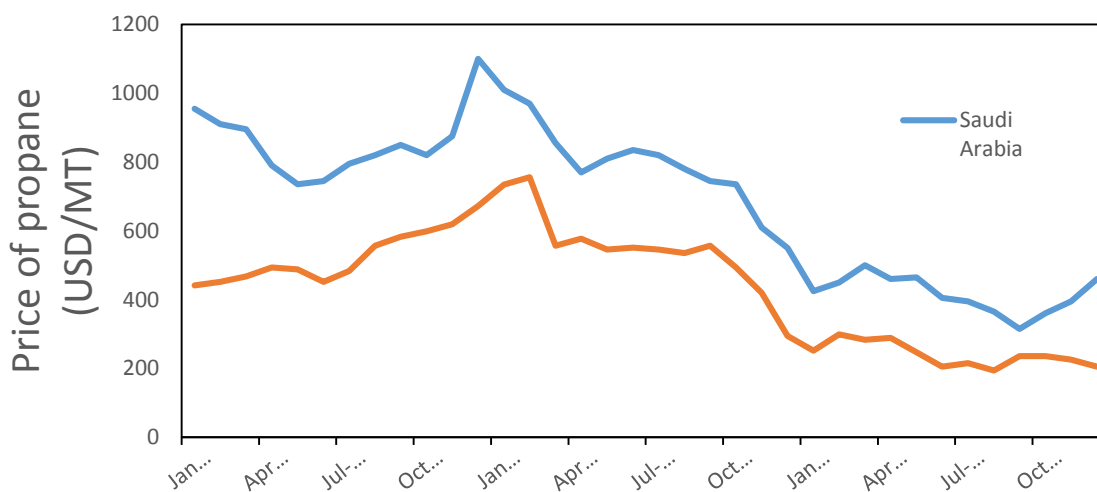
Figure 3 – Cost of propane in Saudi Arabia and Texas, USA from 2013 to 2015

Consequently, it was concluded that the plant could be constructed in North America, most specifically the United States, due to a combination of low raw material costs and proximity to target toluene markets. Moreover, the plant could be close to main water streams in order to provide easy exportation routes to international customers.

Figure 4 – Plant location (adapted from swiftmaps.com)

1.5 Production Methods

There are many synthesis pathways which may be taken to produce toluene. Naphtha reforming consists of a series of endothermic reactions. A platinum catalyst must be used to convert the crude oil feedstock to aromatic compounds. Typical operating conditions for the reactor are 520°C and 1,400 kPa [11]. The aromatization of liquefied petroleum gases is very similar to the naphtha reforming process, however the feedstock consists of lighter hydrocarbons, typically propane and butane, and a ZSM-5 zeolite catalyst. A less commonly used synthesis process is the methylation of benzene, which employs benzene and methanol as feedstock. The process typically operates at pressures and temperatures ranging from 30-35 atm and 340-380°C, respectively [12].

1.5.1 Conventional Naphtha Reforming

The most common production method of toluene is the catalytic reforming of naphtha [4]. Naphtha is a crude oil fraction composed mainly of naphthenes, paraffins and aromatics [13]. Its composition varies depending on the crude oil used and on the way the naphtha was obtained [13]. Most of the toluene is produced from straight run light naphtha [4], which is the naphtha recovered directly from the crude distillation column [13]. Light naphtha is defined as the

fraction boiling between 30°C and 90°C, whereas heavy naphtha is the fraction boiling between 90°C and 200°C [13]. Naphtha can also be produced from heavier distillate fractions [13].

Hydrotreating precedes the catalytic reforming of naphtha. In this step, the petroleum fraction and recycled hydrogen react in a catalyst bed. A separator vessel and a stripper are required to recover hydrogen and hydrotreated naphtha. The latter is sent to the catalytic reforming process where it goes through a series of catalytic reactors [4]. Since the reaction is endothermic, the reactors are surrounded by interstage heat furnaces. The reactor inlet is typically at 520°C and 1,400 kPa [11]. A platinum catalyst is regenerated and recycled [14]. The product stream is sent to a flash drum and to a stabilizer to recover hydrogen and the reformate [4].

Pyrolysis gasoline undergoes the same hydrotreating process as naphtha before being hydrogenated a second time. The treated pyrolysis gasoline is then mixed with the treated naphtha and the stream is sent to the toluene recovery process. A depentanizer and a distillation column remove molecules lighter than C_6 and heavier than o-xylene. To recover the aromatic products, the stream is sent to an extractor, a stripper and in some cases an extractive distillation unit (depending on the number of products to be recovered). The aromatic stream is finally fed to a series of distillation towers to recover toluene, with a purity of 99.8% [4]. The naphtha process typically has an aromatic yield of approximately 60% [15].

1.5.2 Methylation of Benzene

The methylation of benzene is another reactive pathway to synthesize toluene. Commercial applications of this process date back as far as 1942 where a commercial plant was constructed in Waldenburg (now Walbrzych), Poland. This process used benzene and methanol as feedstock, and the reaction was carried out at pressures and temperatures ranging from 30-35 atm and 340-380°C, respectively [12]. The reactor effluent was then cooled in a condenser and separated in a vessel. The gas separated from this vessel was compressed and cooled to recover the benzol. The liquid from the vessel contained two phases: the aqueous phase was distilled to recover the unreacted methanol for recycling, while the hydrocarbon phase was sent to a series of packed columns and distillation columns to finally achieve nitration grade [12].

In 1976 it was discovered that acidic zeolites play an important role in the transformation of methanol to hydrocarbons (MTH) process [16]. The reactivity of methanol in the presence of

zeolites led to various applications, including the methylation of benzene. The reaction of benzene with methanol leads to various co-products such as xylene, ethylbenzene, cumene and n-propylbenzene [17]. However, it was found that reducing the contact time between the methanol and the benzene would suppress any side reactions. The process was shown to achieve a toluene selectivity of 80% under certain conditions [17].

1.5.3 Aromatization Processes from Liquefied Petroleum Gases

Naphtha feedstock can represent a significant portion of the expenditures associated with the operation of the traditional naphtha reforming processes. Indeed, Al-Zahrani reports that cost of raw materials for the traditional process can reach up to 80% of the production costs [18]. As a consequence of the high operating costs associated with the process, significant efforts have been invested in finding alternative routes for large-scale production of aromatics, especially by large multinationals such a British Petroleum (BP), Universal Oil Products (UOP) or Mitsubishi Oil [18]. These efforts have resulted in the design of processes that can make use of liquefied petroleum gases (LPGs). LPGs, byproducts of refining operations and extraction from oil and gas fields, consist mainly of propane and butane, which are low-value [19].

These processes were developed for the common purpose of enabling the use of LPGs as feedstock, and was made possible through advances in catalysis [18], and especially through the formulation of the ZSM-5 zeolite catalyst by Argauer and Landolt [20]. However, they differ in some key aspects such as the type of reactor used, the type of catalyst used and the catalyst regeneration method.

It was found in literature that acidic zeolite catalysts, such as ZSM-5, are subject to deactivation caused by acid-site poisoning, more specifically the formation of coke in hydrocarbon reactions. However, ZSM-5 shows a higher resistance to deactivation compared to other types of zeolites due to its low acid site density and smaller pore size. The deactivation and coke formation mechanisms are not yet fully understood, but it was determined that the amount of coke and catalyst deactivation rate are proportional to the reaction conversion rate. However, ZSM-5 remains one of the most commonly used catalysts in reactions such as hydrocarbon cracking and alkene oligomerization[21].

1.5.3.1 The M2-Forming Process

The development of processes designed to convert LPGs to aromatics follow the introduction of the M2-forming process by Mobil. In a study published in 1986 [22], Mobil proposed the use of the HZSM-5 catalyst, based on the ZSM-5 catalyst, as a solution to the long-standing problem regarding the aromatization of light (C_5 and lighter) hydrocarbons. The HZSM-5 catalyst, a zeolite composed of SiO_2/Al_2O_3, is capable of converting hydrocarbons as light as propane to aromatics with yields proportional to the reaction temperature [22]. The study also strongly emphasizes the fact that HZSM-5 is very stable due to its resistance to coking. It also emphasizes its ability to withstand repeated cycles of regeneration in an oxidative environment, which is inevitable because of catalyst deactivation. Although this process was not designed to convert LPGs, the discovery of the catalyst laid the groundwork upon which other multinationals developed sophisticated processes to upgrade LPGs.

1.5.3.2 The Cyclar Process

Around the same time, in 1984, British Petroleum (BP) and UOP announced the development of the Cyclar process designed specifically to convert LPGs to aromatics [23]. This process, similarly to the M2-forming process, makes use of a proprietary ZSM-5 based catalyst doped with gallium [18]. The feed and the main products in this process are in the liquid phase [19], which makes it particularly convenient for handling. The main reaction is carried out adiabatically in a vertical stack of reactors with external interstage heating [23], [18]. The process implements the usage of the CCR (Continuous Catalyst Regeneration) technology for regenerating the catalyst; the catalyst flows down the reactors by gravity, after which it is regenerated in a CCR regenerator unit, which is economically advantageous [18]. The Cyclar process was first implemented in one of BP's refinery in Grangemouth, Scotland between 1990 and 1991, after which its operations were stopped because of "poor process economics" [24]. It was operating with a capacity of 1,000 barrels per day (BPD) [24] and had an aromatic yield of 65 wt%, 27% of which were for toluene. The Cyclar process had reactor operating conditions of 500-550°C and 100-135 kPa [23]. A large-scale plant owned by the Saudi petrochemical corporation Sabic operates the Cyclar process at a capacity of approximately 45,000 BPD since 1999 in Yanbu, Saudi Arabia [24], [25].The ongoing operation of the Cyclar process in Saudi

Arabia supports the idea that it may be an economically viable process depending on factors such as the proximity of LPG sources.

1.5.3.3 The Aroforming Process

The *Institut français du pétrole* (IFP) and the Australian company SALUTEC introduced the Aroforming process, a process similar to BP/UOP's Cyclar process in terms of catalyst and operating conditions [18]. This process uses zeolite catalysts (such as ZSM-5) doped with a metal oxide such as Ga_2O_3 [18] and is highly flexible in terms of the nature of the feedstock and the production scale [18]. Contrarily to the Cyclar process, the reaction is carried out isothermally in alternating fixed bed tubular reactors, such that when one is in operation, the catalyst in the other can be regenerated [18]. This process was never deployed for large-scale production of aromatics, although a small-scale plant was built in 1994 [26].

1.5.4 Other Relevant Processes

Other processes have been designed, notably the Z-Forming process by Mitsubishi Oil and Chiyoda Corp. The process uses a system of switching reactors in conjunction with a metallosilicate zeolite to generate BTX species from LPGs or light naphtha [18]. This technology was employed by Nippon Oil, but its use was discontinued in 2008, as yields were considered to be unsatisfactory [26]. The process also forms large amounts of hydrogen and fuel gas [18] which are of relatively low value.

Sanyo and Asahi Co. developed the Alpha process to convert C_3-C_7 compounds to aromatics. Contrarily to the other processes, this process performs best when the feedstock is enriched in alkenes instead of the alkanes, which are usually preferred in other processes such as Cyclar [18].

1.6 Process Selection

The most common route for producing toluene and other petrochemical-grade aromatics remains the conventional catalytic reforming process from naphtha [27]. As aforementioned, other options have been explored in the last 30 years and have shown that it is not the only economically viable route to produce toluene. The Cyclar process developed by UOP/BP was

selected for the proposed toluene plant based on various factors, including the feedstock and its associated cost.

The cost of raw materials is pivotal in determining the economic viability of the process [28], as it constitutes a very large portion of the operating costs. LPGs are reputed for being of low value. In Europe, for example, ethylene manufacturers have reported consistently higher profit margins since 2012 with LPG feedstock as opposed to naphtha [29]. Figure 5 illustrates the ethylene profit margins over the first quarter of 2015. The increase in profit margins for ethylene with LPG feedstock is an indicator that the margins could be higher for toluene as well as both processes use the same feedstock.
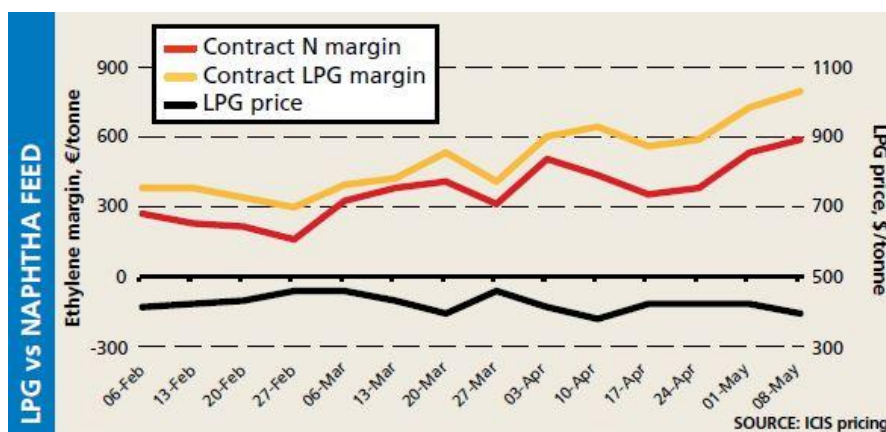
Figure 5 – Comparison of the ethylene margins using LPG and naphtha as feedstock for the first 2015 quarter [29]

Recent reports also indicate that there is currently a general shift toward the use of LPGs in the Asian petrochemical industry due to its lower cost [30], although the price of naphtha has momentarily gained momentum for a short period in 2015 [31]. However, it is important to note that the market price of these chemicals appears to be volatile and may vary depending on their availability.

Another consideration that favours LPG-dependent processes is their flexibility. This family of processes can operate with different feedstock including light naphtha [32]. This flexibility allows for a greater latitude in how the process is operated, and allows for the usage of either feedstock depending on the state of the market. This is particularly relevant given the volatile market.

The lifetime and stability of the catalyst is also a strong factor to consider, often due to its high cost of purchase. The HZSM-5 zeolite used as a catalyst in the Cyclar process has been reported to have a long lifetime and to be more stable and resistant to coking than the catalysts used in conventional naphtha reforming [33]. Furthermore, the Cyclar process also regenerates the catalyst with its continuous catalyst regeneration (CCR) technology, which consists essentially in calcination of coke deposits on the catalyst in a regeneration unit. CCR permits to bypass the need for alternating reactors seen in all other technologies.

The catalyst undergoes a series of steps inside the regeneration unit. These steps include calcination, where the coke is burnt at high temperatures (approximately 400°C), redistribution of the doping metals in the catalyst through chloride addition and drying [13].
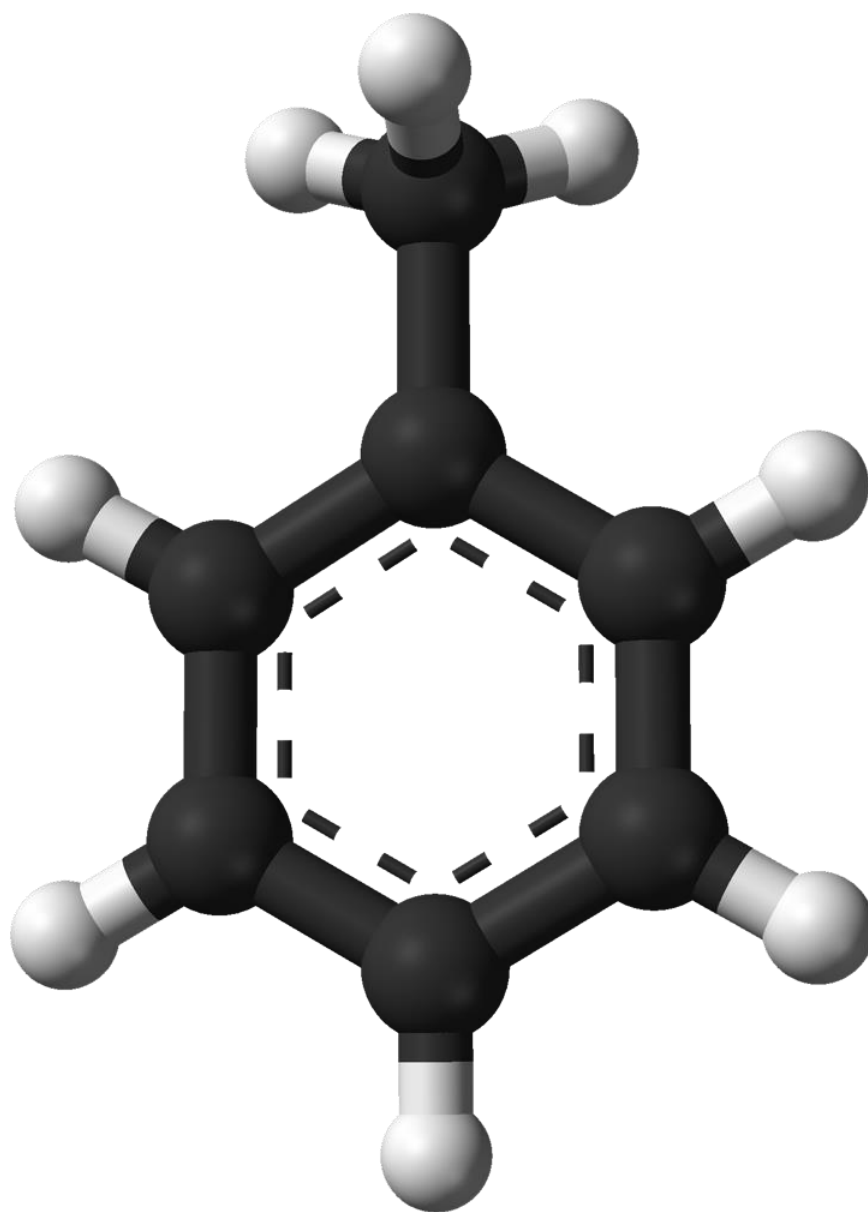
The simplicity of the process and reaction system is also a major consideration for process design, and LPG-based processes are simpler. First, the LPG feedstock, which consists of propane, butane or a mixture of both, significantly reduces the network of possible side-reactions. In contrast, naphtha is a rather complex mixture of hydrocarbons with varying composition depending on the source [13].

The availability of experimental data concerning the reactions can also severely limit the possible design options. Due to the proprietary nature of the LPG-based processes, very little data is available for the reaction kinetics in many of the processes considered. Corbetta *et al.* published a complex kinetic model of over 79 reactions for the aromatization of propane on H-ZSM-5, which is the reaction used in the Cyclar process [34]. Kinetics data for the other LPG aromatization processes is not readily available, likely because it is proprietary information.

Therefore the price and availability of the raw materials, the simplicity of the reaction system, the long catalyst lifetime and the access to a kinetic model are all factors that led to the decision of investigating the Cyclar process.

CHAPTER 2
PROCESS DESCRIPTION

2.1 Process Overview

2.1.1 Raw Materials

Due to a lack of experimental data concerning the kinetics of aromatization of butane at scales larger than bench-scale and for design simplification purposes, the use of pure propane as feedstock is proposed. Even though butanes achieve slightly higher yields (66% versus 62%) [33], it is worth noting that propane is generally less costly than butane [35] and that the increase in yield with butane as feedstock may or may not justify its higher cost.

Propane is widely available, although its cost has been variable. In the Middle East, Saudi Aramco, based in Dhahran, Saudi Arabia, is one of the leading LPG provider and exporter. North America also produces important quantities of LPG due to its shale gas extraction operations [36].

Propane feedstock is available at relatively high purities. The propane supplied by Saudi Aramco is at least 95% pure [37]. The remaining 5% consists of butanes (4%) and olefins (alkenes). This feedstock can, for all intents and purposes, be considered pure, because butane is an alternative feedstock to propane and because olefins are intermediates in the aromatization reaction [33]. The Canadian supplier Superior Propane provides propane with a similar composition [38], suggesting that high purity propane is readily available in these two regions.

2.1.2 By-Products and Co-Products

The Cyclar process is often described as a "dehydrocyclodimerization" reaction [33] and consists of a reaction network which leads to the formation of numerous co-products and by-products as seen in Figure 6.

Figure 6 – Dehydrocyclodimerization of propane on a zeolite catalyst [39]

Hydrogen is an important co-product of toluene and is a result of the first and limiting step of the dehydrocyclodimerization reaction, the dehydrogenation of propane. This reaction also yields a propene intermediate, another co-product of the toluene synthesis process [39].

As the propene intermediate accumulates on the catalyst, it oligomerizes to form longer alkenes, which may take two routes [39]. The alkene oligomers may undergo cracking and yield methane and ethane as by-products. Alternatively, the oligomers may form aromatic cycles such as toluene, benzene and xylenes (by-products) via dehydrocyclization [39]. Other heavier aromatics with nine carbons or more are also produced in small quantities representing roughly 9% of the total aromatic yield in a theoretical Cyclar process with recycle [33]. Other by-products (ethylene, butene, C_4-C_6 alkanes, ethylbenzene, naphthalenes) are formed in relatively small amounts corresponding to roughly 5% of the total product (for a single pass).

Fortunately, there is a market for many of the by-products and co-products produced in the Cyclar process. In fact, benzene and xylenes are often more valuable than toluene itself and toluene is often valorized to benzene via hydrodealkylation [2].

The fuel gas generated via cracking contains hydrogen, methane and ethane. This may be used as a fuel for the fired heaters designed for interstage heating along the reactor stack, while the remainder can be sent to a flare.

2.1.3 Reaction Conditions and Kinetics

To help determine the optimal reaction pathway, an analysis on its complexity, the reaction spontaneity and kinetics is conducted. The analysis of these parameters help ensure that the chosen reaction pathway leads to a simpler system, which may help reduce costs associated to the production of the chemical in question.

2.1.3.1 Reaction Spontaneity

Reaction spontaneity is one of the many factors used to assess the feasibility of a reaction pathway. It is evaluated using the Gibbs free energy (ΔG). The ΔG of the system is thermodynamically related to the equilibrium constant, as shown in Equation 2-1:

$$\Delta G^o_{f\,298} = \overset{n\,products}{\underset{i}{\sum}} a_i \Delta G^o_{f,i\,298} - \overset{n\,reactants}{\underset{j}{\sum}} a_j \Delta G^o_{f,j\,298} \qquad\qquad (2\text{-}1)$$

Where a_x is the stoichiometric coefficient of species X and $\Delta G^o_{x,f,\,298}$ is the change of Gibbs free energy of formation of species X at 298 K and 1 atm.

This equation only provides the reaction spontaneity at room temperature, which is not useful because it does not specify optimal operating conditions. The van't Hoff equation can be rearranged to obtain the equilibrium constant at any given temperature (Equation 2-2). This equilibrium constant can be used in conjunction with Equation 2-3 to find the change in Gibbs free energy at temperature 2:

$$K_2 = e^{\frac{-\Delta H^o_{f,298}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \qquad\qquad (2\text{-}2)$$
$$\Delta G^T = -RTln(K_2) \qquad\qquad (2\text{-}3)$$

From Equation 2-2, it can be concluded that for lower ΔG the equilibrium reaction favours the products.

To conduct the analysis on reaction spontaneity, it is necessary to know what compounds are involved. The aromatization of propane is considered a complex set of reactions. Corbetta *et al.* described this reaction system using 79 different reaction steps. The overall limiting reaction is the dehydrogenation of propane to propene [40]. The propane dehydrogenation can be described by the following chemical reaction [34]:

$$C_3H_8 + C_2H_4 \rightarrow C_3H_6 + C_2H_6 \qquad\qquad \text{Reaction 1}$$

Figure 7 depicts the reaction spontaneity as a function of reaction temperature.
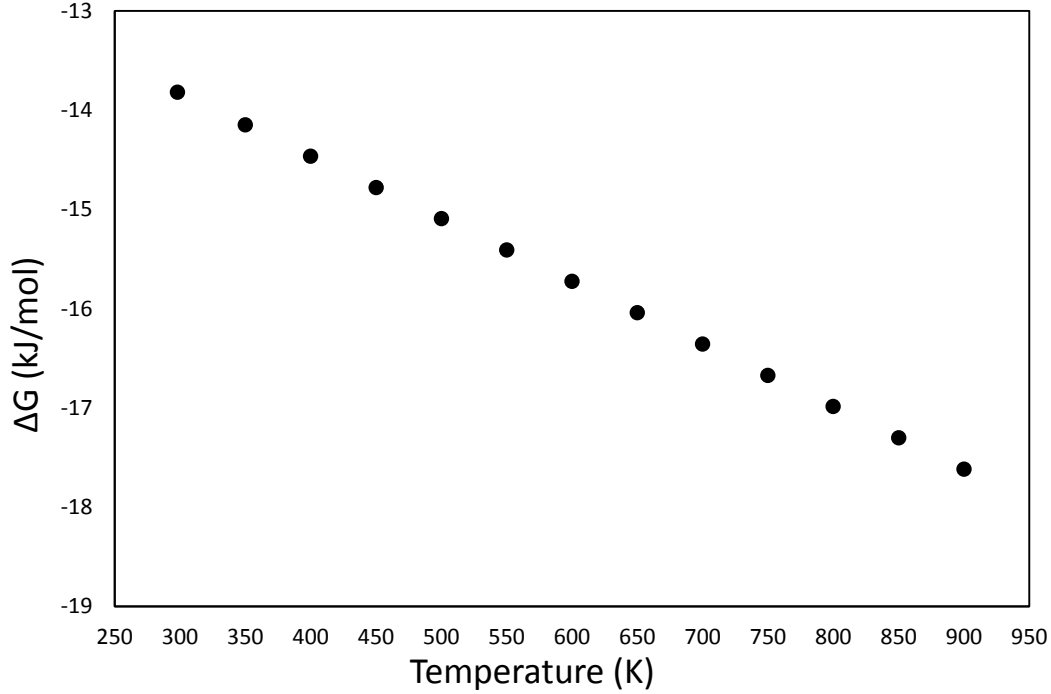
Figure 7 – Dependence of Gibbs free energy on temperature for propane dehydrogenation on H-ZSM-5 catalyst

Figure 7shows that the Gibbs free energy is inversely proportional to the reaction temperature. In general, the reaction is worth considering if the change in Gibbs free energy is low or negative. Thus, the limiting reaction step can be considered spontaneous in the range of 500-550°C, which is the temperature range proposed by Corbetta *et al.* However as the temperature increases, so does the spontaneity.

2.1.3.2 Reaction Catalysis and Kinetics

Corbetta *et al.* [34] studied the kinetics of the aromatization of propane with H-ZSM-5, the protonated form of ZSM-5. ZSM-5 is a medium pore zeolite used in the aromatization of alkanes [18]. This catalyst is widely used due to its small pore size as well as the low acid site density, which greatly reduces the catalyst deactivation from coking [18]. The reaction rates can be simplified to Equation 2-4, assuming that the adsorption and desorption steps are not the rate-limiting steps [34]:

$$r_j = k_j \prod_{m=1}^{n} P_m \qquad (2\text{-}4)$$

15

The kinetic constants for all 79 reactions were modeled as the Arrhenius expression, described by Equation 2-5:

$$k_j = A_0 e^{\frac{-E_a}{RT}}$$

<div align="right">(2-5)</div>

The full list of the pre-exponential factor and the activation energy for every reaction is found in Appendix A of Volume 2.

2.1.4 Block Flow Diagram

While a complete description of the process and its operating conditions will follow in Section 2.2, the block flow diagram of the process is presented in Figure 8 as a quick overview of the process. The propane feed is heated and depressurized to the reaction conditions before entering the reactor. The reactor effluent is then cooled and sent to a flash vessel, where BTX (benzene, toluene and benzene) liquid stream exits from the bottom. The gas stream, containing mainly hydrogen, propane and fuel gas is sent to a distillation tower to recover the remaining BTX. These aromatics are then mixed with the flash vessel exit BTX stream. The gas stream exiting the distillation tower is sent to a second distillation tower to recover propane. A fraction of the propane is recycled back into the feed preparation stream, where it is mixed with the fresh propane stream, while another fraction is purged to avoid accumulation in the system. The combined BTX stream is processed in a series of distillation columns, in which the benzene, toluene and xylenes are separated.
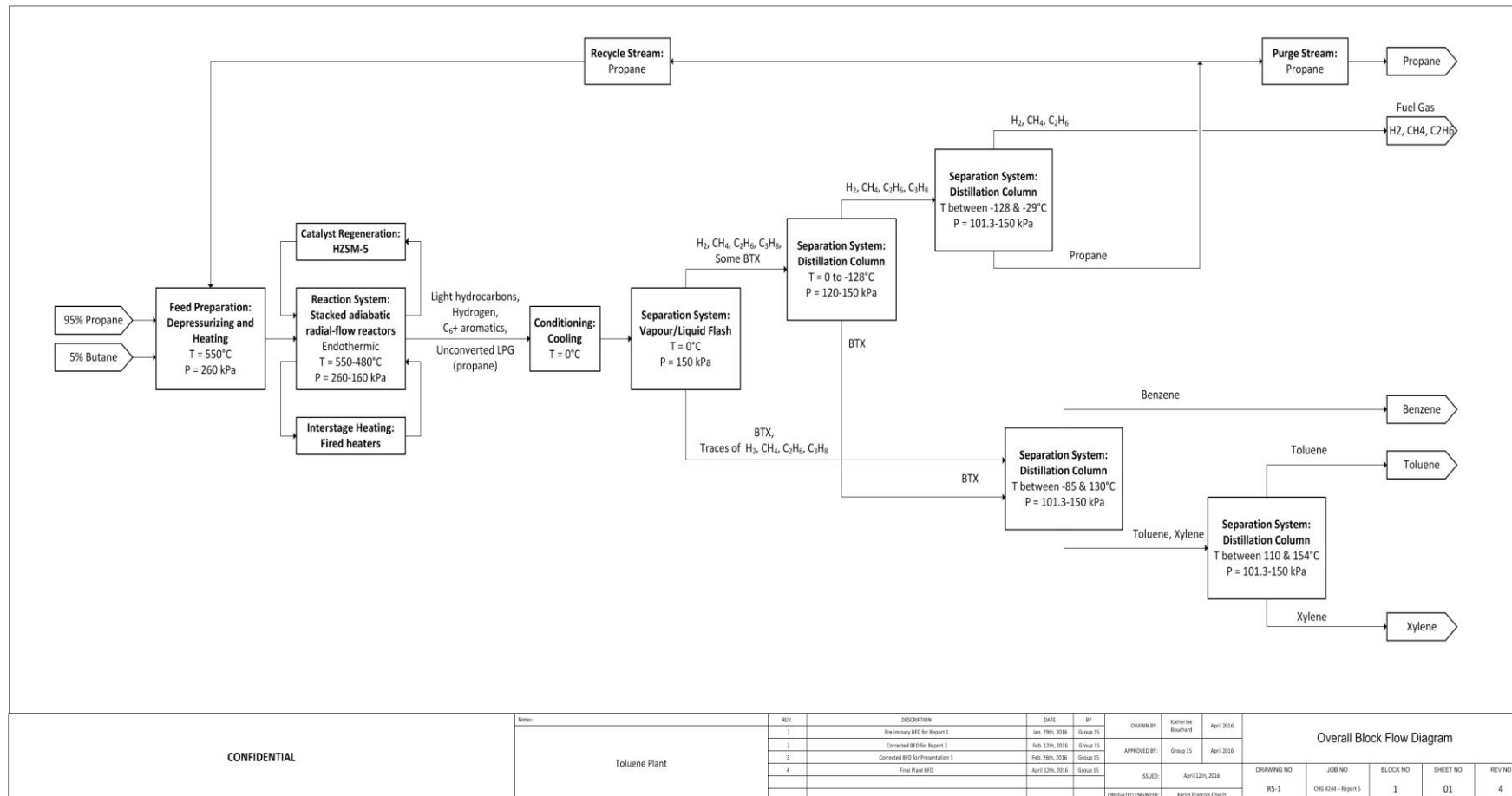
Figure 8 – Block flow diagram of the toluene production process

2.1.5 Overall Plant Material Balance

An overall plant material balance was generated by means of a UniSim simulation. The overall material balance can be found in Table 1.

Table 1 – Plant overall material balance

Compound	Inlet Mass Flow Rate (MT/yr)	Outlet Mass Flow Rate (MT/yr)
Feed		
Propane	189,000	391
Butane	13,100	138
Products		
Toluene	-	50,340
Xylenes	-	24,379
Benzene	-	24,379
By-Products/Co-Products		
Methane	-	69,000
Ethane	-	24,000
Hydrogen	-	5,400
Ethylene	-	3,380
Pentane	-	119
Hexane	-	65.4
Hexene	-	22.8
Butene	-	21.1
Pentene	-	18.4
Propene	-	15.1
Octane	-	14.4
Octene	-	6.5
Heptane	-	0.06
Heptene	-	0.02

From Table 1, it can be seen that 4124 kg of propane is consumed per hour. The production rate of toluene is 1095.8 kg/h.

2.1.6 Preliminary Cost Estimate

In Saudi Arabia, the price of propane has been following a decreasing trend over the last three years (2013-2015) as shown in Figure 9, and sells for 345 USD per metric ton as of January 2016. The propane price in Mt. Belvieu, TX is considered representative of the North American market [41] and closed at 205 USD per metric ton in December 2015 [42].
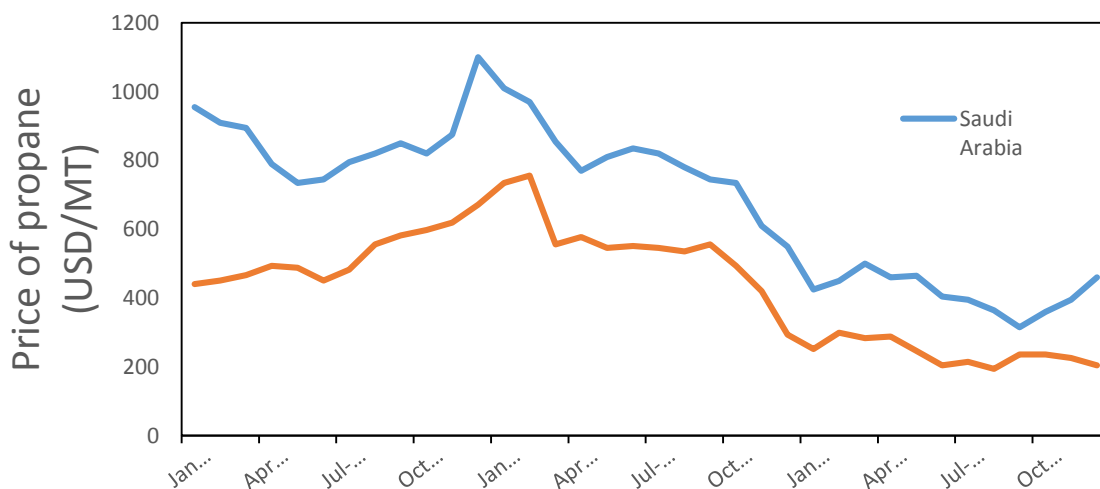
Figure 9 – Price of propane in North America and Saudi Arabia over the 2013-2015 period. (Generated from published prices [42], [35])

When assessing the viability of a process, a simple economic analysis is conducted to have a simple estimation of profits. The estimation of profits in calculated by Equation 2-6:

$$Profitability = \sum_{i}^{products} C_i \times \dot{m}_i - \sum_{j}^{raw\ materials} C_j \times \dot{m}_j \qquad (2\text{-}6)$$

However, to conduct the preliminary profitability analysis, a mass balance is needed. The mass flows of raw materials, products, the cost of every chemical species and the estimated cash flow can be found in Table 2.

Table 2 – Simulation mass flows, prices and cash flows for the propane aromatization process [43], [44], [28]

Compound	Mass Input (MT/yr)	Mass Output (MT/yr)	Chemical Price (USD/MT)	Cash flow (USD/yr)
Propane	2.03×10^5	-	345	-6.99×10^7
Toluene	-	5.02×10^4	669	3.36×10^7
Benzene	-	2.47×10^4	740	1.83×10^7
Xylene	-	2.51×10^4	825	2.07×10^7
Fuel gas	-	1.02×10^5	N/A	N/A
Total	2.03×10^5	2.02×10^5	N/A	2.68×10^6

From Table 2, it can be concluded that with a propane feed of 2.03×10^5 MT/yr, a cash flow of $2.68M is calculated from the aromatization of propane. The preliminary analysis of the process leads to the conclusion that it may be economically viable.

2.2 Detailed Design Description

2.2.1 Feed Preparation and Reaction System

The process flow diagram of the feed preparation and reaction system (PFD 100) is presented in Figure 10. The feed, which is delivered to the process at 25°C and 912 kPa, is depressurized to 290 kPa through valve VL-101. It is then mixed with the recycle streams from Sections 300 (PFD 300) and heated to 550°C in heat exchanger HX-101 and fired heater FH-101. It is then sent to the stacked reactors, which are represented by the reactor R-101. The reactor operates at 550-467°C and 260-161 kPa. The ranges are due to pressure drop through the reactor and to the fact that the reactions are endothermic. A continuous catalyst regeneration (CCR) system, RG-101, operates alongside the reactor.
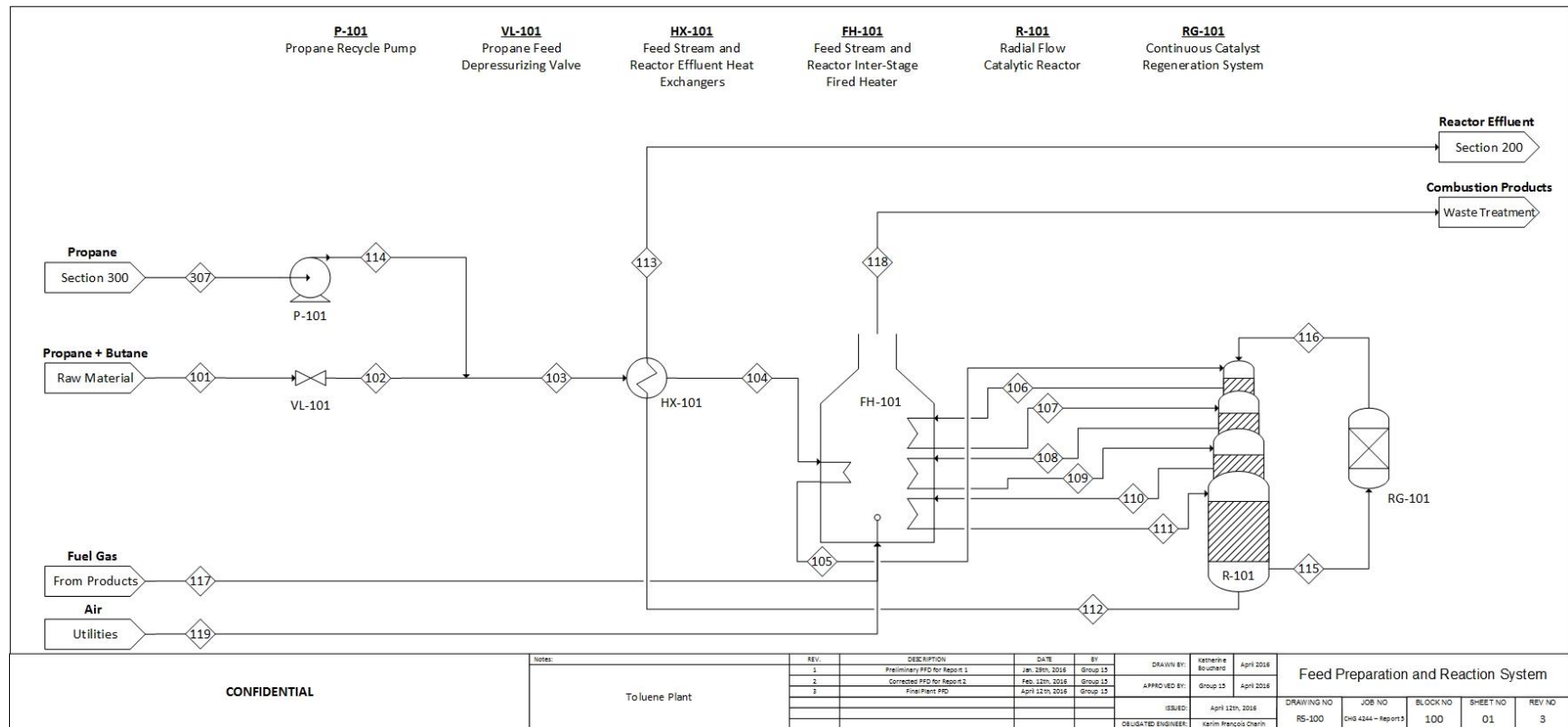
Figure 10 – PFD 100 (Feed Preparation and Reactor System)

Table 3 – Process stream table for Section 100 (Feed Preparation and Reactor System)

Process Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction									
					H2	CH4	C2H6	C2H4	C3H8	C3H6	C4H10	C4H8	C5H12	C5H10
101	24041	25.0	912.3	0.00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.35E-01	0.00E+00	6.49E-02	0.00E+00	0.00E+00	0.00E+00
102	24041	-13.5	290.0	0.25	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.35E-01	0.00E+00	6.49E-02	0.00E+00	0.00E+00	0.00E+00
103	24434	-13.5	290.0	0.25	6.87E-34	1.50E-24	1.02E-05	1.97E-11	9.32E-01	4.10E-04	6.61E-02	3.96E-04	7.32E-04	1.28E-04
104	24434	453.0	280.0	1.00	6.87E-34	1.50E-24	1.02E-05	1.97E-11	9.32E-01	4.10E-04	6.61E-02	3.96E-04	7.32E-04	1.28E-04
105	24434	550.0	260.0	1.00	6.87E-34	1.50E-24	1.02E-05	1.97E-11	9.32E-01	4.10E-04	6.61E-02	3.96E-04	7.32E-04	1.28E-04
112	24368	481.0	161.0	1.00	2.63E-02	3.36E-01	1.17E-01	1.65E-02	1.37E-02	4.84E-04	2.99E-03	4.99E-04	1.31E-03	2.18E-04
113	24368	0.0	151.0	0.89	2.63E-02	3.36E-01	1.17E-01	1.65E-02	1.37E-02	4.84E-04	2.99E-03	4.99E-04	1.31E-03	2.18E-04
307	392	-28.7	150.0	0.00	4.17E-32	9.36E-23	6.35E-04	1.22E-09	7.30E-01	2.55E-02	1.44E-01	2.46E-02	4.55E-02	7.97E-03
114	393	-28.5	420.0	0.00	4.27E-32	9.35E-23	6.34E-04	1.22E-09	7.30E-01	2.55E-02	1.44E-01	2.46E-02	4.55E-02	7.96E-03

Table 3 Continued – Process stream table for Section 100 (Feed Preparation and Reactor System)

Process Stream	Mass Flow (kg/h)	Temperature (°C)	Pressue (kPa)	Vapour Fraction	Mass Fraction									
					Hexane	Hexene	Heptane	Heptene	Octane	Octene	Benzene	Toluene	Xylenes	O2
101	24041	25.0	912.3	0.00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
102	24041	-13.5	290.0	0.25	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
103	24434	-13.5	290.0	0.25	9.40E-05	4.23E-05	1.23E-11	9.18E-12	6.37E-14	9.40E-14	2.17E-04	1.30E-09	7.54E-16	0.00E+00
104	24434	453.0	280.0	1.00	9.40E-05	4.23E-05	1.23E-11	9.18E-12	6.37E-14	9.40E-14	2.17E-04	1.30E-09	7.54E-16	0.00E+00
105	24434	550.0	260.0	1.00	9.40E-05	4.23E-05	1.23E-11	9.18E-12	6.37E-14	9.40E-14	2.17E-04	1.30E-09	7.54E-16	0.00E+00
112	24368	481.0	161.0	1.00	4.03E-04	1.52E-04	3.04E-07	1.14E-07	6.99E-05	3.17E-05	1.19E-01	2.45E-01	1.20E-01	0.00E+00
113	24368	0.0	151.0	0.89	4.03E-04	1.52E-04	3.04E-07	1.14E-07	6.99E-05	3.17E-05	1.19E-01	2.45E-01	1.20E-01	0.00E+00
307	392	-28.7	150.0	0.00	5.24E-03	2.51E-03	1.32E-09	7.94E-10	6.28E-11	6.95E-11	1.35E-02	1.19E-06	1.20E-11	0.00E+00
114	393	-28.5	420.0	0.00	5.85E-03	2.63E-03	7.67E-10	5.71E-10	3.96E-12	5.84E-12	1.35E-02	8.07E-08	4.69E-14	0.00E+00

Table 4 – Utilities stream table for Section 100 (Feed Preparation and Reactor System)

Utilities Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction											
					H2	CH4	C2H6	C2H4	C3H8	C3H6	C4H10	C4H8	C5H12	C5H10	C6H14	C6H12
117	910.3987673	-121.6	101.3	0.99	3.39E-01	5.44E-01	1.00E-01	1.52E-02	9.22E-04	3.66E-05	1.16E-04	2.06E-05	2.93E-05	5.28E-06	2.83E-06	1.38E-06
118	43413.03005	560.0	101.3	1.00	1.42E-03	2.28E-03	4.21E-04	6.37E-05	3.87E-06	1.53E-07	4.86E-07	8.65E-08	1.23E-07	2.22E-08	5.93E-08	2.90E-08
119	42502.83	25.0	101.3	1.00	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03

Table 4 Continued – Utilities stream table for Section 100 (Feed Preparation and Reactor System)

Utilities Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction										
					C7H16	C7H14	C8H18	C8H16	Benzene	Toluene	Xylenes	Oxygen	Nitrogen	Water	Carbon dioxide
117	910.3987673	-121.6	101.3	0.99	6.10E-13	3.74E-13	2.54E-14	2.86E-14	8.04E-06	5.98E-10	5.24E-15	0.00E+00	0.00E+00	0.00E+00	0.00E+00
118	43413.03005	560.0	101.3	1.00	1.28E-14	7.84E-15	5.33E-16	6.01E-16	1.69E-07	1.25E-11	0.00E+00	1.41E-01	7.49E-01	7.47E-02	3.08E-02
119	42502.83	25.0	101.3	1.00	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.42E-03	2.35E-01	7.65E-01	1.42E-03	1.42E-03

2.2.2 Reactor Effluent Separation Process

The process flow diagram for the preliminary separation process (PFD 200) is presented in Figure 11. The reactor effluent is cooled down in heat exchangers HX-101 before being sent to the flash vessel V-201, where C_6 and heavier aromatics are liquefied while most light hydrocarbons (such as ethane and methane), hydrogen and unconverted LPG remain in the vapour phase. The operating conditions of the flash vessel V-201 are 151 kPa and 0°C in order to achieve a proper separation.

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V-201
Flash Vessel for Initial
Separation of Light
Hydrocarbons and Aromatics

H_2, C_1-C_3,
Some BTX

201 → Section 300

Reactor Effluent

Section 100 — 113 → V-201

BTX and Traces
of H_2, C_1-C_3

202 → Section 400

Notes:	REV.	DESCRIPTION	DATE	BY	DRAWN BY:	Katherine Bouchard	April 2016					
	1	Preliminary PFD for Report 1	Jan. 29th, 2016	Group 15					Flash Separation			
CONFIDENTIAL	2	Corrected PFD for Report 2	Feb. 12th, 2016	Group 15	APPROVED BY:	Group 15	April 2016					
Toluene Plant	3	Final Plant PFD	April 12th, 2016	Group 15								
					ISSUED:	April 12th, 2016		DRAWING NO	JOB NO	BLOCK NO	SHEET NO	REV NO
					OBLIGATED ENGINEER:	Karim François Charih		R5-200	CHG 4244 – Report 5	200	01	3

Figure 11 – PFD 200 (Reactor Effluent Separation)

26

Table 5 – Process stream table for Section 200 (Reactor Effluent Separation)

Process Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction									
					H2	CH4	C2H6	C2H4	C3H8	C3H6	C4H10	C4H8	C5H12	C5H10
113	24368	0.0	151.0	0.89	2.63E-02	3.36E-01	1.17E-01	1.65E-02	1.37E-02	4.84E-04	2.99E-03	4.99E-04	1.31E-03	2.18E-04
201	13369	0.0	151.0	1.00	4.80E-02	6.12E-01	2.12E-01	2.99E-02	2.43E-02	8.59E-04	4.76E-03	8.13E-04	1.55E-03	2.71E-04
202	11000	0.0	151.0	0.00	3.22E-06	4.74E-04	1.49E-03	1.54E-04	7.07E-04	2.94E-05	8.36E-04	1.18E-04	1.02E-03	1.53E-04

Table 5 Continued – Process stream table for Section 200 (Reactor Effluent Separation)

Process Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction								
					Hexane	Hexene	Heptane	Heptene	Octane	Octene	Benzene	Toluene	Xylenes
113	24368	0.0	151.0	0.89	4.03E-04	1.52E-04	3.04E-07	1.14E-07	6.99E-05	3.17E-05	1.19E-01	2.45E-01	1.20E-01
201	13369	0.0	151.0	1.00	2.39E-04	1.03E-04	6.95E-08	2.53E-08	5.57E-06	2.56E-06	3.85E-02	2.36E-02	2.89E-03
202	11000	0.0	151.0	0.00	6.02E-04	2.10E-04	5.89E-07	2.23E-07	1.48E-04	6.70E-05	2.17E-01	5.14E-01	2.63E-01

2.2.3 Light Ends Recovery

The process flow diagram of propane purification (PFD 300) is presented in Figure 12. The gas stream from Section 200 goes into distillation column T-301 at 151 kPa and 0°C. Remaining BTX is recovered in the column bottoms and sent to the BTX recovery section (Section 400). The unconverted propane is recovered from the hydrogen-rich stream in distillation tower T-302, which operates at 120 kPa and -127.9 °C. It is then partially mixed with the fresh propane feed of the process while 10% is purged to avoid accumulation.
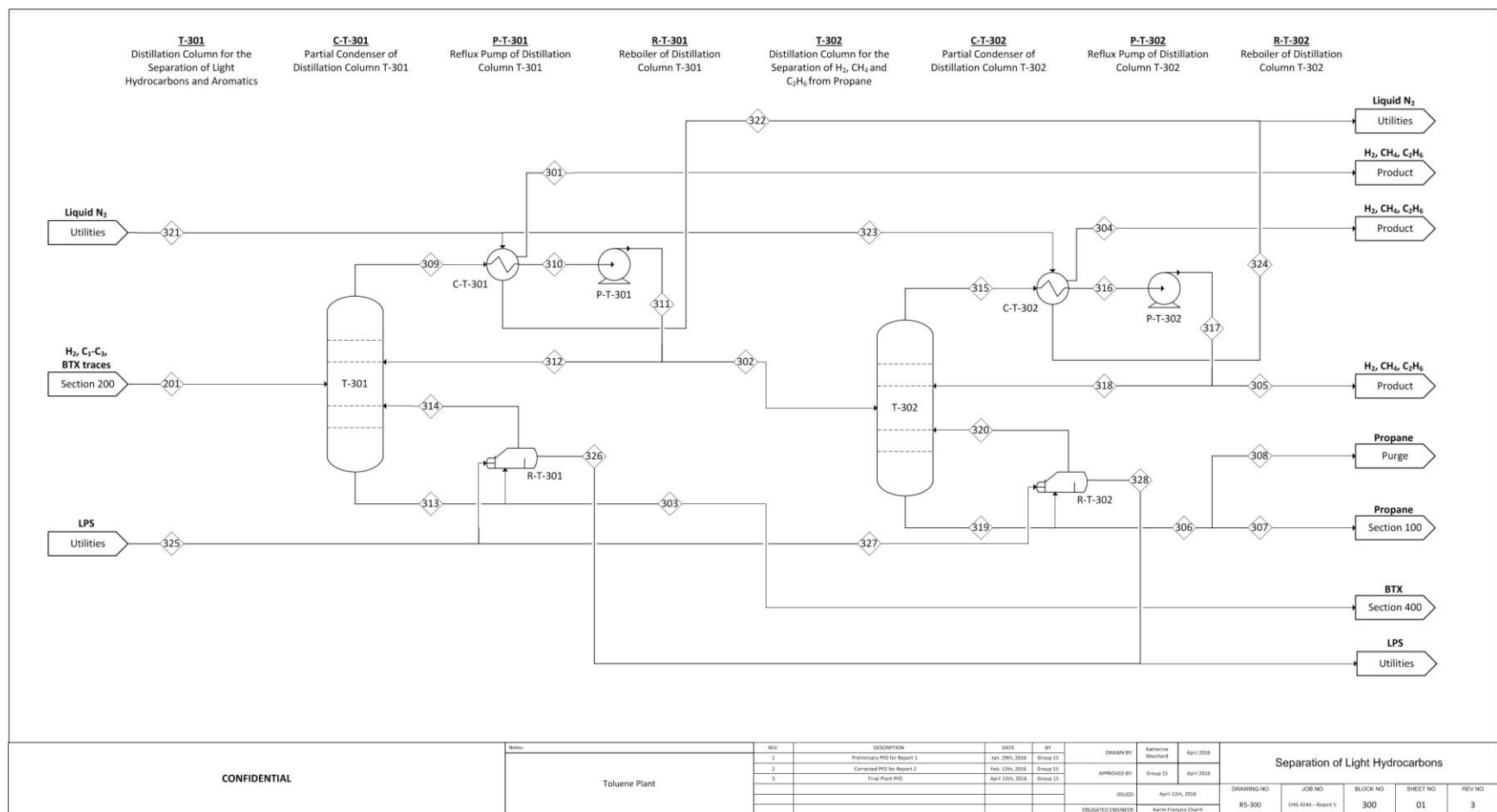
Figure 12 – PFD 300 (Light Ends Separation)

Table 6 – Process stream table for Section 300 (Light Ends Separation)

Process Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction									
					H2	CH4	C2H6	C2H4	C3H8	C3H6	C4H10	C4H8	C5H12	C5H10
201	13369	0.0	151.0	1.00	4.80E-02	6.12E-01	2.12E-01	2.99E-02	2.43E-02	8.59E-04	4.76E-03	8.13E-04	1.55E-03	2.71E-04
301	10154	-127.9	120.0	1.00	6.32E-02	7.98E-01	1.11E-01	2.77E-02	5.95E-04	3.06E-05	4.26E-06	1.10E-06	4.30E-08	1.48E-08
302	2348	-127.9	120.0	0.00	7.96E-06	3.64E-02	7.27E-01	5.04E-02	1.36E-01	4.75E-03	2.67E-02	4.58E-03	8.46E-03	1.48E-03
303	867	100.6	150.0	0.00	1.77E-21	5.83E-13	9.03E-07	1.17E-08	5.27E-04	2.59E-05	9.30E-04	1.32E-04	1.05E-03	1.76E-04
304	1894	-91.1	101.3	1.00	9.86E-06	4.51E-02	8.93E-01	6.22E-02	1.02E-04	9.56E-06	1.39E-09	9.69E-10	3.16E-14	3.56E-14
305	17	-91.1	101.3	0.00	4.43E-09	1.37E-03	9.70E-01	2.66E-02	1.47E-03	1.06E-04	2.36E-07	1.16E-07	6.24E-11	4.36E-11
306	436	-28.7	150.0	0.00	4.17E-32	9.36E-23	6.35E-04	1.22E-09	7.30E-01	2.55E-02	1.44E-01	2.46E-02	4.55E-02	7.97E-03
307	392	-28.7	150.0	0.00	4.17E-32	9.36E-23	6.35E-04	1.22E-09	7.30E-01	2.55E-02	1.44E-01	2.46E-02	4.55E-02	7.97E-03
308	44	-28.7	150.0	0.00	4.17E-32	9.36E-23	6.35E-04	1.22E-09	7.30E-01	2.55E-02	1.44E-01	2.46E-02	4.55E-02	7.97E-03

Table 6 Continued – Process stream table for Section 300 (Light Ends Separation)

Process Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction								
					Hexane	Hexene	Heptane	Heptene	Octane	Octene	Benzene	Toluene	Xylenes
201	13369	0.0	151.0	1.00	2.39E-04	1.03E-04	6.95E-08	2.53E-08	5.57E-06	2.56E-06	3.85E-02	2.36E-02	2.89E-03
301	10154	-127.9	120.0	1.00	2.18E-10	2.62E-10	2.69E-18	1.74E-18	6.22E-21	1.12E-20	8.82E-10	5.41E-15	1.27E-21
302	2348	-127.9	120.0	0.00	9.73E-04	4.66E-04	2.46E-10	1.47E-10	1.17E-11	1.29E-11	2.51E-03	2.21E-07	2.23E-12
303	867	100.6	150.0	0.00	1.05E-03	3.31E-04	1.07E-06	3.90E-07	8.58E-05	3.96E-05	5.88E-01	3.63E-01	4.45E-02
304	1894	-91.1	101.3	1.00	4.95E-19	3.81E-18	2.31E-29	2.09E-29	3.97E-30	3.86E-30	4.73E-18	2.06E-25	3.69E-30
305	17	-91.1	101.3	0.00	9.54E-15	3.58E-14	4.02E-24	3.28E-24	3.21E-28	1.02E-27	6.54E-14	1.98E-20	6.69E-29
306	436	-28.7	150.0	0.00	5.24E-03	2.51E-03	1.32E-09	7.94E-10	6.28E-11	6.95E-11	1.35E-02	1.19E-06	1.20E-11
307	392	-28.7	150.0	0.00	5.24E-03	2.51E-03	1.32E-09	7.94E-10	6.28E-11	6.95E-11	1.35E-02	1.19E-06	1.20E-11
308	44	-28.7	150.0	0.00	5.24E-03	2.51E-03	1.32E-09	7.94E-10	6.28E-11	6.95E-11	1.35E-02	1.19E-06	1.20E-11

Table 7 – Utilities stream table for Section 300 (Light Ends Separation)

Utilities Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction	
					Nitrogen	Water
321	20428	-196.0	101.3	0.00	1.00E+00	0.00E+00
322	20428	-122.0	86.3	1.00	1.00E+00	0.00E+00
323	1453	-196.0	101.3	0.00	1.00E+00	0.00E+00
324	1453	-100.0	86.3	1.00	1.00E+00	0.00E+00
325	218	134.4	308.2	1.00	0.00E+00	1.00E+00
326	218	134.4	308.2	0.00	0.00E+00	1.00E+00
327	818	134.4	308.2	1.00	0.00E+00	1.00E+00
328	818	134.4	308.2	0.00	0.00E+00	1.00E+00

2.2.4 Aromatics Separation

The process flow diagram for the BTX recovery process (PFD 400) is presented in Figure 13. The combined BTX stream from Section 200 and Section 300 is depressurized through valve VL-401 to 130 kPa and 8.19°C and then sent to a first distillation tower, T-401, that allows to recover benzene as a distillate. The remaining aromatics are depressurized to 131 kPa and 126.2 °C through valve VL-402. The stream is sent to the second distillation tower, T-402, to separate toluene and xylenes.
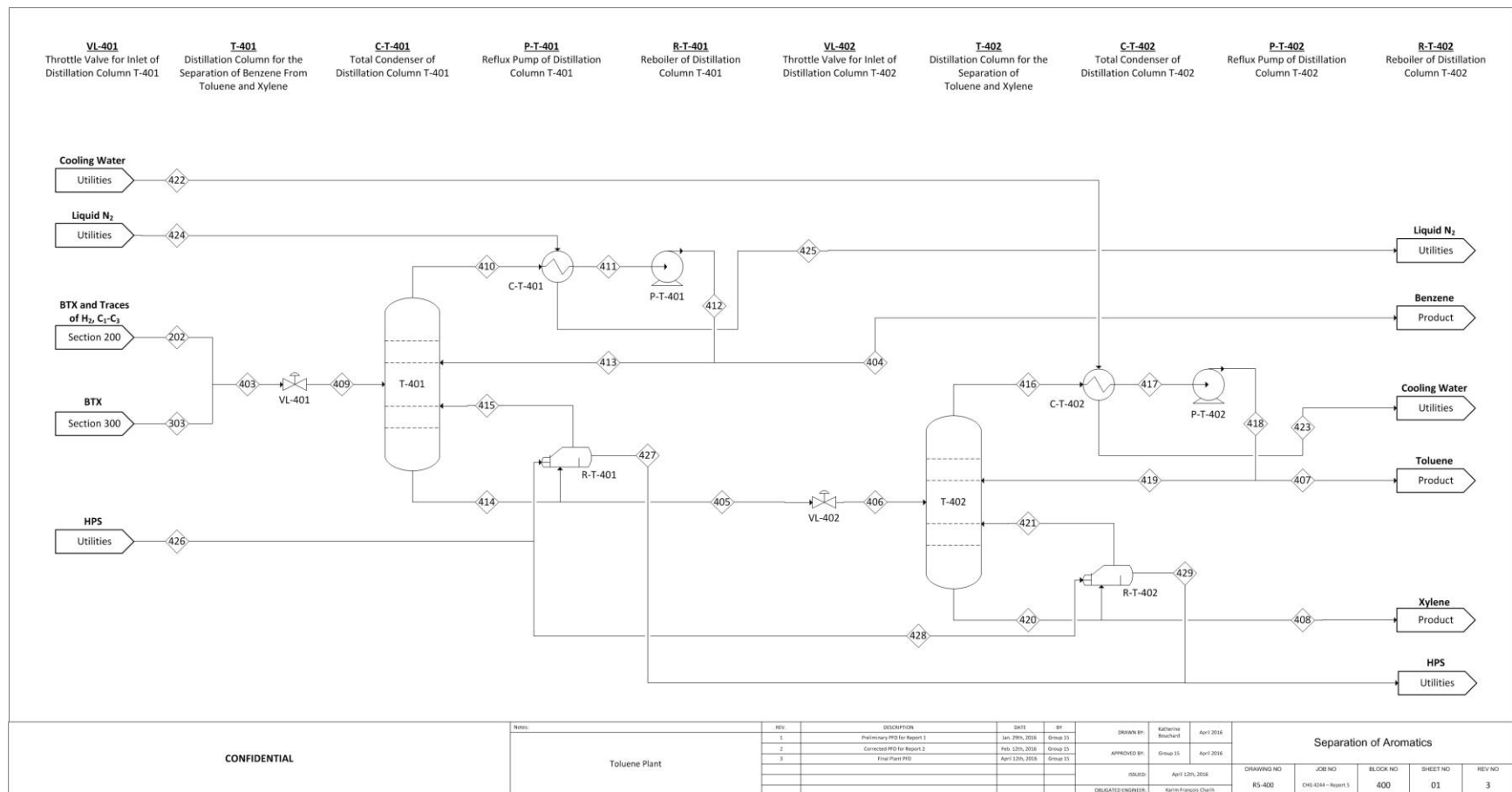
Figure 13 – PFD 400 (Aromatics Separation)

Table 7 – Process stream table for Section 400 (Aromatics separation)

Process Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction									
					H2	CH4	C2H6	C2H4	C3H8	C3H6	C4H10	C4H8	C5H12	C5H10
202	11000	0.0	151.0	0.00	3.22E-06	4.74E-04	1.49E-03	1.54E-04	7.07E-04	2.94E-05	8.36E-04	1.18E-04	1.02E-03	1.53E-04
303	867	100.6	150.0	0.00	1.77E-21	5.83E-13	9.03E-07	1.17E-08	5.27E-04	2.59E-05	9.30E-04	1.32E-04	1.05E-03	1.76E-04
404	2927	-84.9	101.3	0.00	0.00E+00	1.78E-03	5.61E-03	5.80E-04	2.82E-03	1.18E-04	3.42E-03	4.84E-04	4.16E-03	6.26E-04
405	8940	131.3	150.0	0.00	0.00E+00	1.66E-31	3.32E-25	4.05E-27	2.87E-21	2.95E-22	7.33E-16	2.96E-17	8.31E-12	4.37E-13
406	8940	126.2	131.0	0.03	0.00E+00	1.66E-31	3.32E-25	4.05E-27	2.87E-21	2.95E-22	7.33E-16	2.96E-17	8.31E-12	4.37E-13
407	5957	109.8	101.3	0.00	0.00E+00	1.73E-31	4.99E-25	6.07E-27	4.31E-21	4.43E-22	1.10E-15	4.45E-17	1.25E-11	6.55E-13
408	2983	153.5	150.0	0.00	0.00E+00	1.51E-31	2.84E-31	2.65E-31	4.17E-31	3.98E-31	1.48E-27	2.46E-29	1.06E-20	2.26E-22
409	11866	8.2	130.0	0.00	0.00E+00	4.39E-04	1.38E-03	1.43E-04	6.94E-04	2.92E-05	8.43E-04	1.19E-04	1.03E-03	1.54E-04

Table 7 Continued – Process stream table for Section 400 (Aromatics separation)

Process Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction									
					Hexane	Hexene	Heptane	Heptene	Octane	Octene	Benzene	Toluene	Xylenes	Hexane
202	11000	0.0	151.0	0.00	6.02E-04	2.10E-04	5.89E-07	2.23E-07	1.48E-04	6.70E-05	2.17E-01	5.14E-01	2.63E-01	6.02E-04
303	867	100.6	150.0	0.00	1.05E-03	3.31E-04	1.07E-06	3.90E-07	8.58E-05	3.96E-05	5.88E-01	3.63E-01	4.45E-02	1.05E-03
404	2927	-84.9	101.3	0.00	2.58E-03	8.89E-04	2.18E-06	8.36E-07	2.98E-06	2.06E-06	9.69E-01	8.42E-03	2.92E-07	2.58E-03
405	8940	131.3	150.0	0.00	4.57E-08	3.64E-09	1.14E-07	3.85E-08	1.90E-04	8.56E-05	6.47E-03	6.65E-01	3.28E-01	4.57E-08
406	8940	126.2	131.0	0.03	4.57E-08	3.64E-09	1.14E-07	3.85E-08	1.90E-04	8.56E-05	6.47E-03	6.65E-01	3.28E-01	4.57E-08
407	5957	109.8	101.3	0.00	6.85E-08	5.46E-09	1.71E-07	5.78E-08	2.76E-04	1.26E-04	9.71E-03	9.89E-01	1.15E-03	6.85E-08
408	2983	153.5	150.0	0.00	2.93E-14	7.54E-16	2.38E-11	6.26E-12	1.65E-05	5.77E-06	1.45E-07	1.99E-02	9.80E-01	2.93E-14
409	11866	8.2	130.0	0.00	6.35E-04	2.19E-04	6.24E-07	2.35E-07	1.44E-04	6.50E-05	2.44E-01	5.03E-01	2.47E-01	6.35E-04

Table 8 – Utilities stream table for Section 400 (Aromatics separation)

Utilities Stream	Mass Flow (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction	
					Nitrogen	Water
422	68555	20.0	116.3	0.00	0.00E+00	1.00E+00
423	68555	50.0	101.3	0.00	0.00E+00	1.00E+00
424	14123	-196.0	101.3	0.00	1.00E+00	0.00E+00
425	14123	-73.0	86.3	1.00	1.00E+00	0.00E+00
426	5256	251.3	4000.0	1.00	0.00E+00	1.00E+00
427	5256	251.3	4000.0	0.00	0.00E+00	1.00E+00
428	5256	251.3	4000.0	1.00	0.00E+00	1.00E+00
429	5256	251.3	4000.0	0.00	0.00E+00	1.00E+00

2.3 Process Control Strategy

It is essential that proper process control be implemented in the various sections of the plant in order to maintain high product purity, safe process operation and stable operating conditions. Identification of essential control loops is a requirement for process synthesis, as these loops will require adequate instrumentation. The instrumentation will have an impact on capital costs.

Control loops are indispensable for any process. However, these loops are not included in the process simulation in this work, as the process is simulated at steady state for convenience. Simulating process control in UniSim is possible, but would require use of the dynamic mode option, significantly affecting the complexity of an already complex reaction network and set of components.

2.3.1 Control in the Feed Preparation Section

The flow rate of the liquid propane feedstock can be subject to fluctuations or it may otherwise be desirable to change the quantity of propane fed to the process in order to increase or decrease the total plant capacity. A fail-to-close flow control valve placed upstream of the process, connected indirectly to a flow meter measuring the feed flow rate, allows for flexibility and/or consistency in terms of capacity.

The feed preparation section (PFD 100) of the plant includes a fired heater (FH-101). This unit immediately precedes the reactor (R-101), and it is important that the temperature is increased precisely to the operating temperature in R-101. One can anticipate the possibility of a disturbance in the temperature of the propane feedstock or a need to change the operating temperature in R-101. For these reasons, the implementation of a control loop for temperature around FH-101 is justified.

The heating of propane in FH-101 relies on the combustion of fuel gas (a mix of the process waste streams), a co-product in the reaction scheme of the process. A reasonable control strategy consists of controlling the flow rate of fuel gas provided to the fired heater. The temperature of the propane stream fed to R-101 measured with a temperature element is sent to a controller, which can vary the flow rate of fuel gas with a fail-to-close valve provided to FH-101, in order to counteract disturbances or change the operating temperature in R-101.

2.3.2   Control in the Reactor Section

The reactor (R-101) is the core of the process, and control of its operating conditions is of paramount importance.

Given the fact that R-101 comprises multiple stages, and that the reaction is globally endothermic, much consideration should be given to the temperature throughout the different stages. In fact, the temperature is to be brought back to the reactor inlet temperature in between each stages using a fired heater (FH-101) coupled to R-101. The flow rate of the fuel gas provided to FH-101 can therefore be controlled with a temperature control valve (fail-to-close) in order to ensure that every inter-stage stream is returned to the following reactor stage at 550°C. The temperature is to be monitored after each stage, in order to maintain high reaction rates.

Since a gas is present in the fired heater, the pressure must be monitored and controlled by changing the level of the combustion products exiting the fired heater. The pressure control valve must be fail-to-open, to ensure there would be no pressure build-up inside the fired heater in the case of a failure or process upset.

The pressure inside the reactor must also be monitored such that the reactor effluent remains slightly over atmospheric pressure, as the aromatics yield is higher at low pressures, as well as to avoid a pressure build-up inside the reactor vessel [33]. The pressure is adjusted through the aperture of a pressure control valve located downstream. This fail-to-open pressure control valve will adjust the flow of reactor effluent to maintain a constant pressure inside the reactor.

Figure 14 represents a piping and instrumentation diagram for the controls required around the reactor.
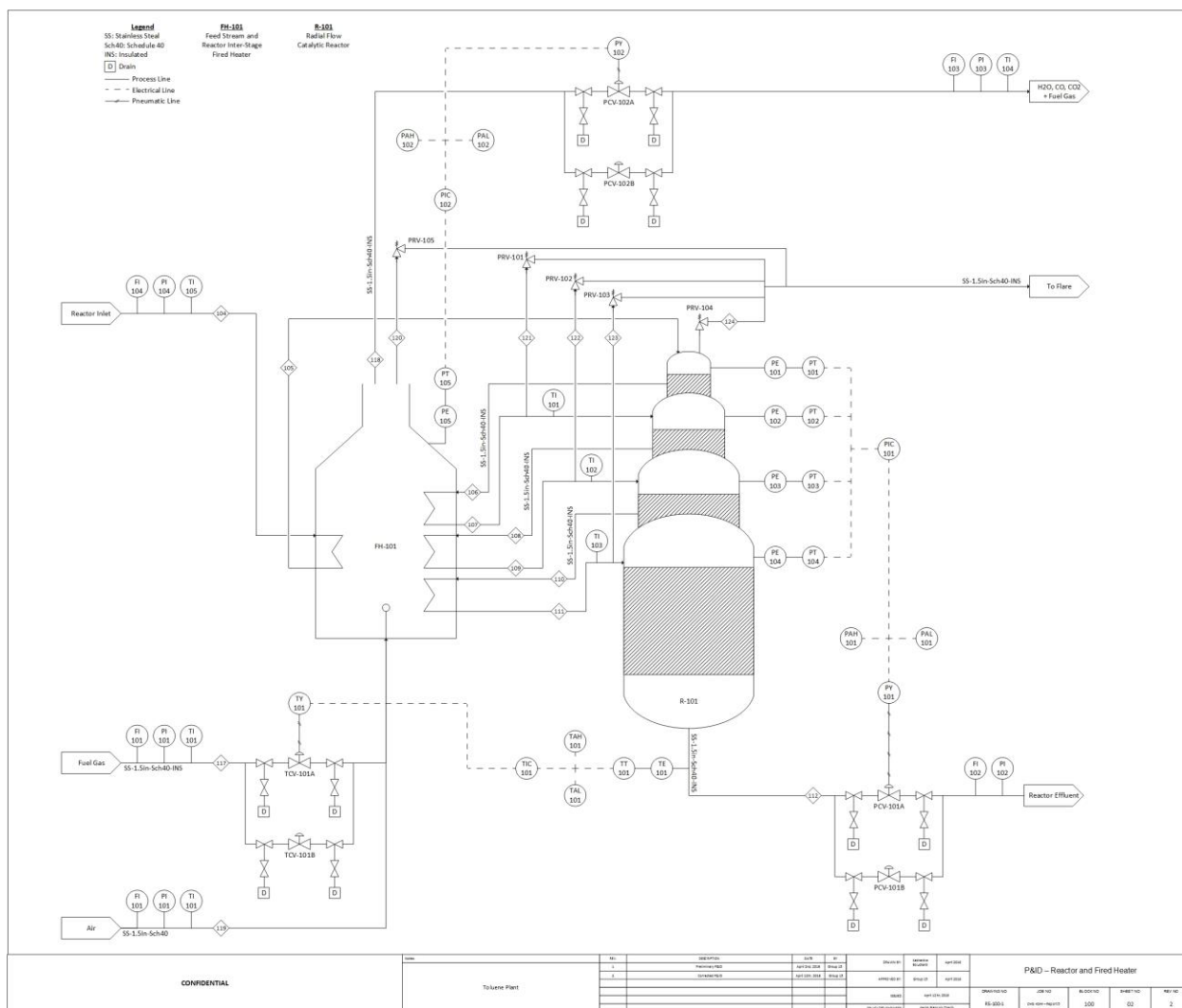
Figure 14 – P&ID of the reactor and fired heater

2.3.3 Control of Downstream Separation Section

The downstream plant section where the product separation is performed comprises many units around which control strategies must be implemented.

The flash vessel (V-201) designed to separate the heavy products (mainly aromatics) from the light products (light hydrocarbons and hydrogen) encloses a two-phase system with liquid and vapour in equilibrium. Pressure build-up in this vessel can be prevented with a pressure relief valve. However, the level of the fluid in the vessel is to be controlled so that there is ample room

in V-201 to achieve a sufficient vapour-liquid separation. A level control valve located downstream prevents an undesirable rise in the level of the liquid in the vessel.

All towers are to be controlled with a common strategy. Variables that are to be controlled include the operating temperature, the operating pressure as well as the liquid level in the lower tower portion and in the reflux drum. Temperatures in the distillate and bottoms streams are controlled by varying the flow rate of cooling fluid and steam in the condenser and reboiler, respectively. The level of liquid is controlled with pumps located downstream, which control the speed of the pump motor drive, in order to increase or decrease the flow of liquid exiting the column. Finally, the pressure inside the distillation column is controlled by a fail-to-open pressure control valve to avoid pressure build-up. This valve allows to adjust the flow of gas exiting the top of the column.

Figure 15 represents a piping and instrumentation diagram for the controls required around distillation columns.
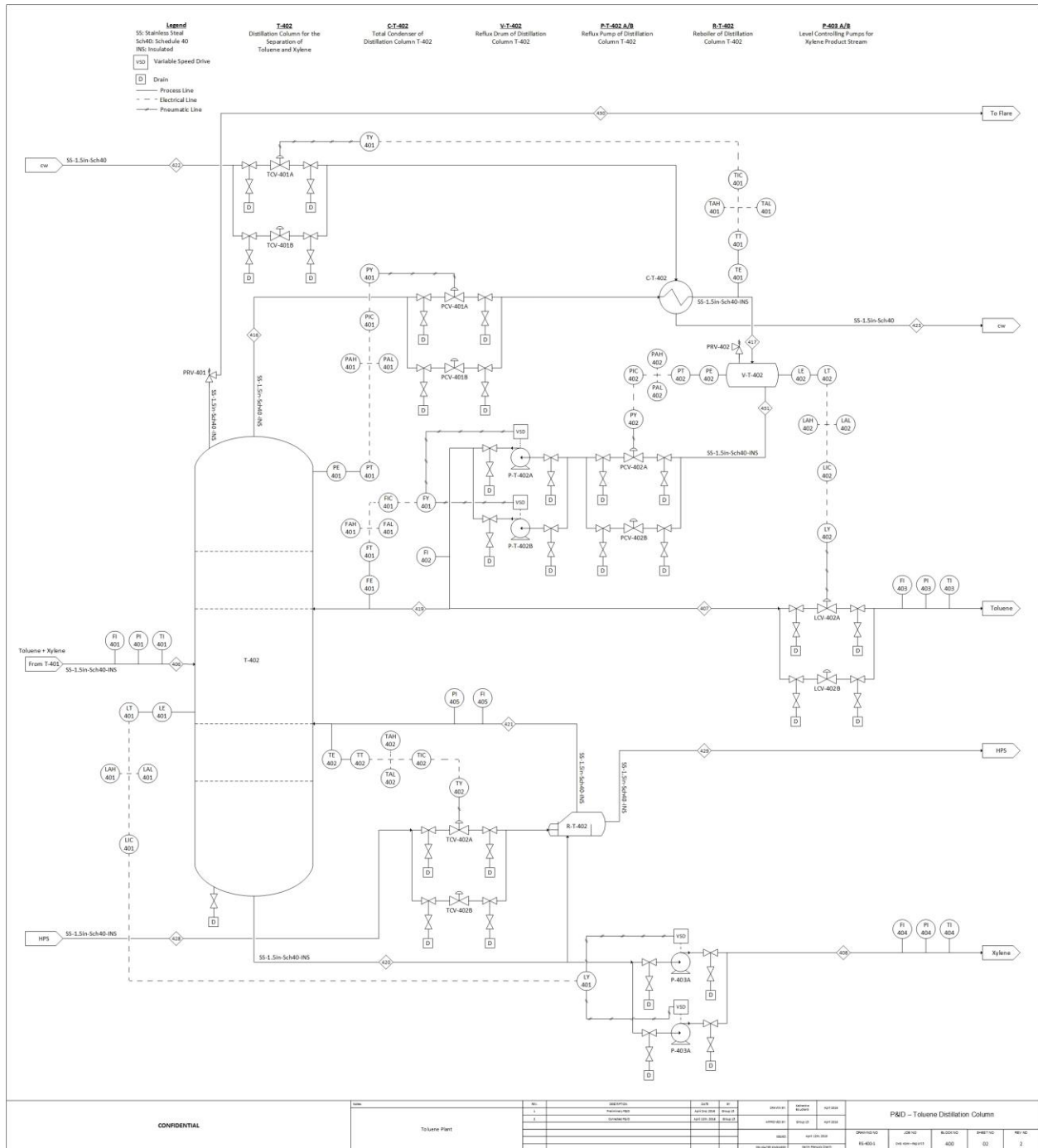
Figure 15 – P&ID of the toluene distillation column

CHAPTER 3
PROCESS AND EQUIPMENT DESIGN

3.1 Thermodynamic Fluid Package Selection

Selecting the optimal thermodynamics model (fluid package) based on the species in the system is crucial. This model dictates the vapour-liquid equilibria (VLE), enthalpies, and pure-species properties in mixtures and will have a significant impact on material and energy balances around individual units and around the entire process [45], [28]. It follows that the reliability of a process simulation is completely dependent on the selection of an appropriate fluid package in the process simulation software [28].

VLE are modeled with equations of state (EOS) or activity-coefficient models (ACM) [28]. The EOS, often derived from the ideal gas law, are reported to provide good results for gases and for light hydrocarbons, while ACMs apply mostly for non-ideal liquid systems involving chemicals below their critical conditions [28].

The aromatization of propane in the Cyclar process involves non-polar hydrocarbons exclusively, providing a rationale for the use of an EOS-based fluid package in unit operations where the species are in gas phase. Turton *et al.* [28] recommend using the Peng-Robinson (PR) or Soave-Redlich-Kwong (SRK) EOS. There is some evidence that both models produce similar results all else being equal [46], although the PR EOS models liquid systems significantly better in exchange of a poorer a predictive ability for polar systems [47], [48].

Corbetta *et al.* selected the SRK EOS to simulate the Cyclar process [34], but failed to provide a satisfactory explanation as to why this particular model was selected instead of PR. It is possible that SRK provides more accurate predictions of experimental data for the process, although this is not explicitly stated.

Given that the process involves non-polar hydrocarbons in both gas-phase and liquid-phase, and based on the lack of a satisfactory justification of the selection of SRK by Corbetta *et al.*, the PR EOS was selected as the fluid package of choice for the process simulation performed in UniSim (Honeywell).

3.2 Feed Preparation

A mixture of 95% propane and 5% butane is delivered to the plant in a pressurized liquid form, but is vapourized for use [49]. It is transported and delivered at ambient temperature. The

minimal pressure at which the propane mixture is in liquid form at 25°C is 912.3 kPa. Therefore, these temperatures and pressures have been assumed as the feed conditions. In order to partially vapourize the propane and lower its pressure, the stream passes through a valve and exits at a pressure of 290 kPa and a temperature of -13.5°C. The propane is then heated to 550°C, which is the reactor temperature, in both a heat exchanger and a fired heater. The first heat exchanger preheats the stream against the reactor effluent, which lowers the duty of the subsequent fired heater. Pressure drops of 10 kPa and 20 kPa have been estimated for the heat exchanger and the fired heater based on heuristics for boiling fluids and gas in heat exchangers [28]. The final pressure of the feed stream, before entering the reactor, is 260 kPa. The design procedure for a heat exchanger is presented in Appendix C.

3.3 Reaction System

The reactor is often considered the core of a chemical process, highlighting the importance of an optimal reactor design. High production volume plants rely on large quantities of feedstock, therefore it is desirable to maximize a set of performance criteria including, among others, conversion, product yield and selectivity for the desired product. Optimized designs decrease the operating costs associated with the process, as smaller feed flow rates are necessary to achieve a given production capacity target. It is important to note, however, that a tradeoff lies between capital and operating costs, as optimized reactor designs may achieve higher conversions, yields and selectivity, but may require significantly larger capital investments. Ultimately, the optimal design should involve the lowest capital and operating costs possible.

Section 3.3 presents the reactor types encountered in the industry, the design procedure for the process of interest, optimization procedures and, finally, the specifications and performance of the selected reactor design.

3.3.1 Reactor

The Radial Flow Moving Bed Reactor (RFMBR) was introduced by Universal Oil Products (UOP) and *Institut français du pétrole* (IFP) in conjunction with their continuous catalyst regeneration (CCR) technology for the catalytic reforming of naphtha [50]. CCR was devised as a response to the large catalyst coking rate that is inherent to catalytic reforming of naphtha for production of reformate and aromatics [13].

In the RFMBR, an annular bed of catalyst flows down by gravity and is sent with a lift gas such as nitrogen or hydrogen to a regeneration unit where the coke deposited on the catalyst is calcinated [33]. The catalyst regeneration involves the burning of the coke, redistribution of the doping metals, chloride addition and drying [13]. The regenerated catalyst is then returned to the top of the bed in the reactor, essentially closing the continuous CCR loop.

A RFMBR and its various flow patterns are presented in Figure 16. The gas flow in a RFMBR is considerably different from than in a typical packed bed reactor (PBR) as a result of the geometry of the moving annular catalyst bed. In RFMBRs, the gas fed to the reactor flows in the radial direction through the annular catalyst bed instead of axially [50]. The benefits of that difference in the flow patterns become evident once the pressure drop through the reactor are considered. Pressure drops are in fact considerably lower in RFMBRs than in PBRs due to the larger area available to the flow [50]. The scaling up of a process in which the reactions are carried out in a PBR will necessitate an increase in the reactor diameter in order to maintain a constant pressure drop (reactor length) [51]. Larger diameters are associated with higher costs, as the reactor must be made thicker in order to support a larger mass of catalyst [51]. In the case of a RFMBR, an increase in capacity only requires an increase in the reactor length which can be achieved at lower costs [51].
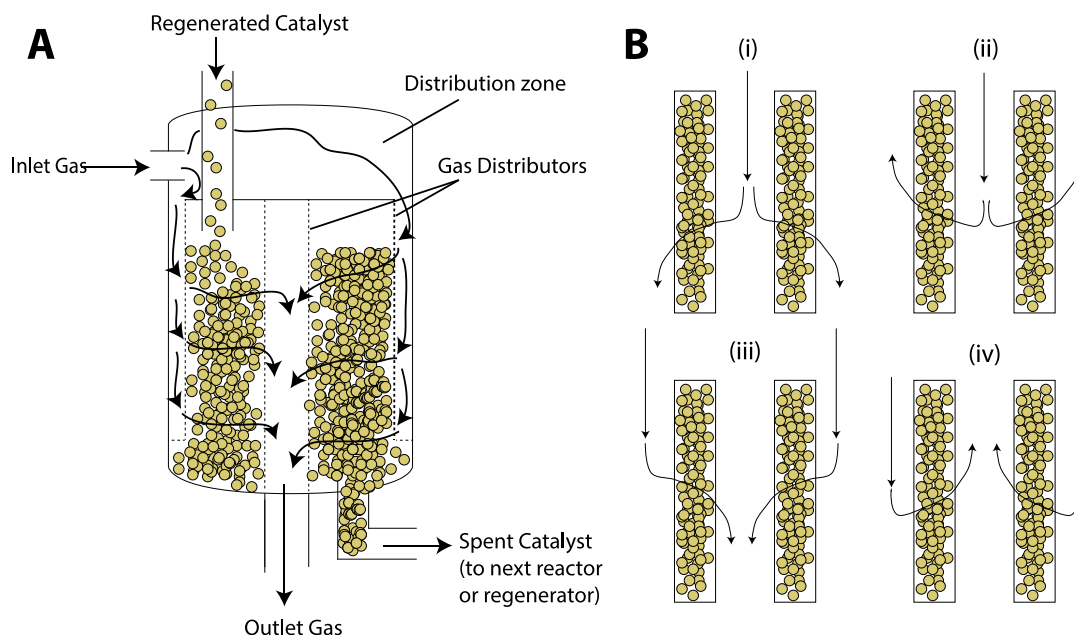
Figure 16 – Radial flow moving bed reactor and its flow patterns

RFMBRs find applications in many different processes in the industry including the synthesis of ammonia, the dehydrogenation of ethylbenzene as well as in the catalytic reforming of naphtha. The lower pressure drop associated with the use of RFMBRs is desirable in the Cyclar process, as lower inlet pressures increase the aromatics yield, although it also increases the requirements in terms of catalyst mass [33].

Due to the endothermic nature of the overall reaction scheme, the reactants are typically reheated in a fired heater and reintroduced into another RFMBR stage [33], [18], [19]. The Cyclar process reactor configuration typically consists of four stacked RFMBR stages, although a series of distinct RFMBR stages in series is also possible and used in UOP's original catalytic reforming process [6]. The mass of catalyst increases from one stage to another to compensate for the decreasing reaction rates caused by the consumption of reactant [51]. The two configurations considered for the process developed here are presented in Figure 17.
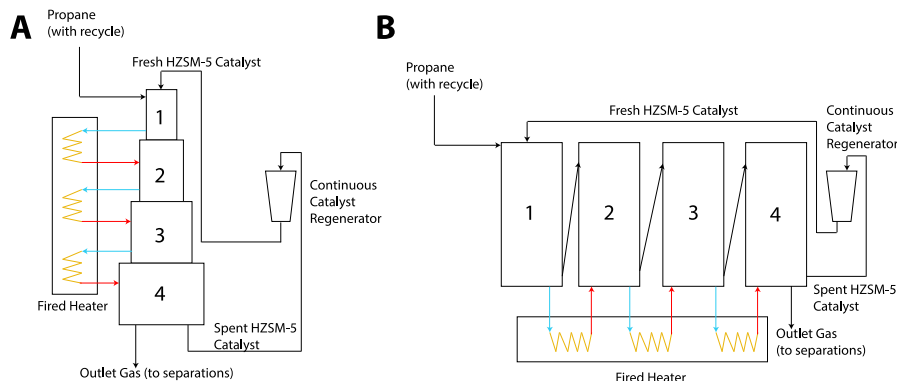
Figure 17 – Common configurations of RFMBR stages

3.3.1.1 *Modelling a Radial-Flow Moving Bed Reactor*

The kinetic scheme presented by Corbetta *et al.* [34] was developed from kinetic data acquired over the 500-550°C temperature, based on the work of Nguyen *et al.* [52] and Bhan *et al.* [53]. From literature, it was anticipated that the process performance would be dependent on the pressure in the reactors [19]. The maximum yield for the production of aromatics is achieved at low pressures because of the minimal hydrocracking occurring at this condition [33]. At high pressures, the proportion of heavy aromatics in the final product is higher [40]. On the other hand, a reaction performed at high pressure uses only half of the catalyst needed compared to the low pressure process [19] because of the increased reaction rate [33]. These considerations

46

highlight the need to perform extensive simulations using an adequate model to optimize process performance (yield, selectivity, conversion) and process economics.

The model describing the evolution of the reaction in this type of reactor has been described in literature [54], and is quite involved. Indeed, the reaction system exhibits a high level of complexity with a total of 79 reactions. Furthermore, these reactions proceed at rates that can vary by many orders of magnitude. Solving for the flow rates of products involves solving an initial value problem (IVP) with a system of ordinary differential equations (ODEs) that comprises one ODE for each species, as well as one for the temperature profile and the pressure profile, for a total of 81 ODEs [55]. Systems of ODEs which vary in order of magnitude are said to be *stiff* and are reported to be particularly difficult to solve using explicit numerical methods for ODE integration such as Euler's method or the classical fourth-order Runge-Kutta method [56]. Solving the system accurately would require step sizes that are prohibitively small, making the methods impractical [57]. Use of implicit numerical methods such as the implicit (or backward) Euler's method, or Gear's backward differentiation formula (BDF) is recommended for these kinds of systems [56]. Corbetta *et al.* report that implementation of such methods should be conducted using an external software (i.e. outside the simulator) [34]. This is in line with the observation that UniSim consistently fails to provide a passable solution to the systems of ODEs in serial reactor stages (initially modelled as PBRs), possibly because its built-in numerical methods cannot handle stiff systems. The issue was reported to the UniSim technical staff who could not suggest an effective solution as of now, although they stated that they would discuss the possible causes of the issue.

Multiple possible solutions have been explored such as a simplification of the reaction scheme (down to about 50 reactions), usage of multiple reactor stages for the reaction scheme, operating condition changes, etc. None have yielded viable results, and no realistic simulation are achieved.

3.3.1.2 Numerical Methods for Stiff Equations

It eventually became obvious that the implementation of a custom simulator would be required in order to properly solve the complex reaction system. MATLAB's ode15s function is a widely used function capable of solving stiff ODEs, but no easy, well-documented way to establish an

interface between MATLAB and Honeywell UniSim could be found. C++ was selected to build a simulator, based on the availability of a suitable numerical library and its ability to interface with UniSim through Visual Basic.

Ultimately, a custom radial-flow moving bed simulator capable of interfacing with UniSim was implemented in C++ and Visual Basic was designed. In addition to providing a solution to the stiff equations, a properly written simulator could yield more accurate results since the reactor design would not have to be modeled as a simple PBR.

3.3.1.3 *Custom Radial-Flow Moving Bed Reactor Simulator*

The complexity of the reaction system raises the issue of stiff ODEs which must be integrated in order to solve for the molar flow rates, temperature and pressure at the reactor outlet. Guido Ferraris-Buzzi developed a numerical library in C++ capable of solving stiff ODE systems by means of Gear's Backward Differentiation Formula (BDF), a predictor-corrector method of fourth-order [58].

Honeywell UniSim provides a set of customization tools and documentation that allow for the development of custom unit operation extensions in Visual Basic. These tools allow to model a unit operation externally and to return the resulting values to UniSim via an object-based model. The lack of suitable numerical libraries in Visual Basic justify the need to build a UniSim-Visual Basic-C++ interface to implement a custom unit operation that can predict the output from the RFMBR. The interface is represented in Figure 18.

Figure 18 – Schematic Representation of the Implementation of the Custom Reactor Extension

The application was developed using the object-oriented paradigm, in order to better reflect the nature of the problem which involves obvious distinct components (streams, reactors, reactions, species, etc.). The unit operation was implemented for standalone use as well as for usage as an

extension in UniSim under the form of a compiled dynamically linked library (DLL). The source code for the standalone simulator is presented in Appendix C.
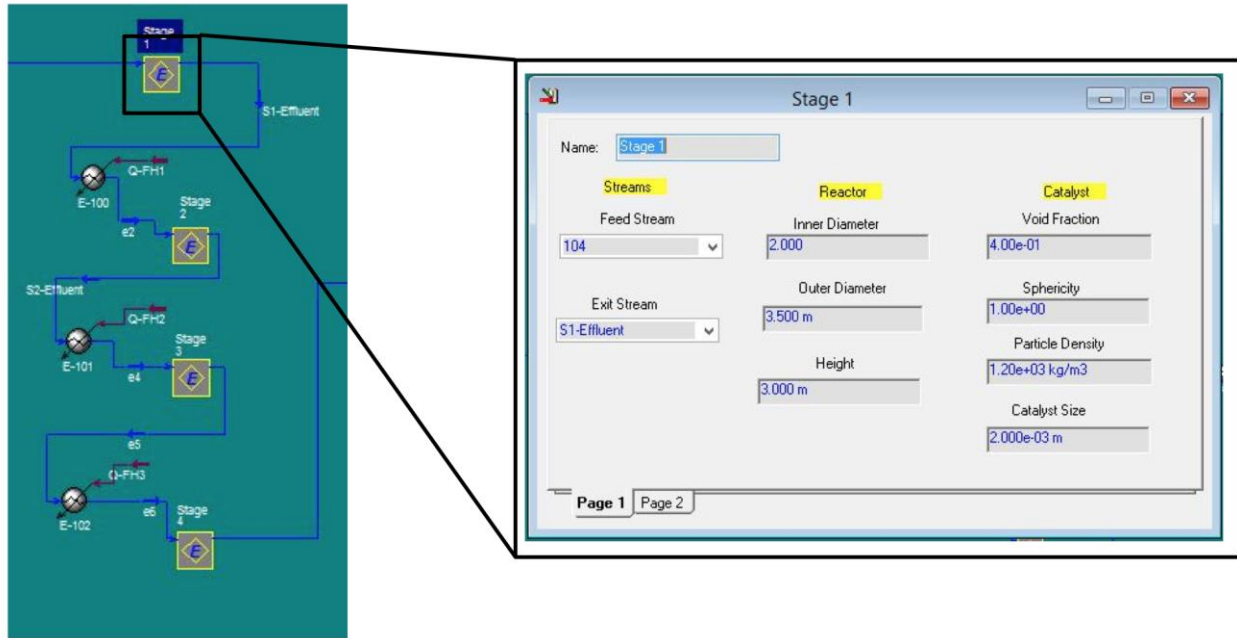
Figure 19 – UniSim interface for the radial-flow moving bed reactor extension

The standalone simulator was used to perform the optimizations and the results obtained were realistic, with a B/T/X ratio similar to that observed by Corbetta *et al.* in similar conditions [34]. The 24/50/26 split observed at the reactor effluent is in excellent agreement with the 26/51/23 split reported in Corbetta *et al.* Furthermore, the fact that the mass is conserved from the inlet to the outlet further supports the validity of the procedure.

To be useful for usage with UniSim, the application must solve a performance problem where the goal is to predict the composition and conditions (temperature and pressure) of the reactor effluent rather than sizing the reactor.

3.3.1.4 Relevant Assumptions and Limitations

To simplify the implementation of the reactor, some assumption had to be made. They are tabulated in Table 9

Table 9 – Assumptions made for the reactor design

Assumption	Relevant Step
Constant gas density equal to that of propane throughout the reactor	Integration of the Ergun equation for the pressure drop
Heat capacities are constant and taken to be the average over the range of plausible temperatures (298 – 900 K)	Integration of the energy balance ODE
All heats of reaction are constant and equal to the standard heats of reaction	Integration of the energy balance ODE
The ideal gas law is applicable	Calculation of the volumetric flow rate of gas for the gas superficial velocity and conversion from concentration to pressure
Catalyst deactivation is negligible/Uniform catalytic activity throughout the catalyst bed	Integration of component flow rate ODEs

These assumptions are more or less reasonable, but had to be made in order to make the reactor design achievable in a timely manner.

3.3.1.5 Final Reactor Design

The design procedure for reactor, initially modelled as a simple PBR, is presented in Appendix C. The updated design procedure for the radial-flow moving bed reactor design is enclosed in the source code of the simulator (see Appendix C).

The final reactor design is presented in Table 10

Table 10 – Final radial-flow moving bed reactor design

	Stage 1	Stage 2	Stage 3	Stage 4
Material of construction	Stainless Steel (Grade 304)	Stainless Steel (Grade 304)	Stainless Steel (Grade 304)	Stainless Steel (Grade 304)
Design pressure (kPa)	260	232	203	168
Height (m)	3.0	4.0	6.0	8.0
Inner diameter (m)	2.0	2.0	1.5	2.0
Outer diameter (m)	3.5	4.0	4.0	5.0
Outer shell diameter (m)	4.0	4.5	4.3	5.4
Mass of catalyst (ton)	13.6	26.4	45.4	92.4
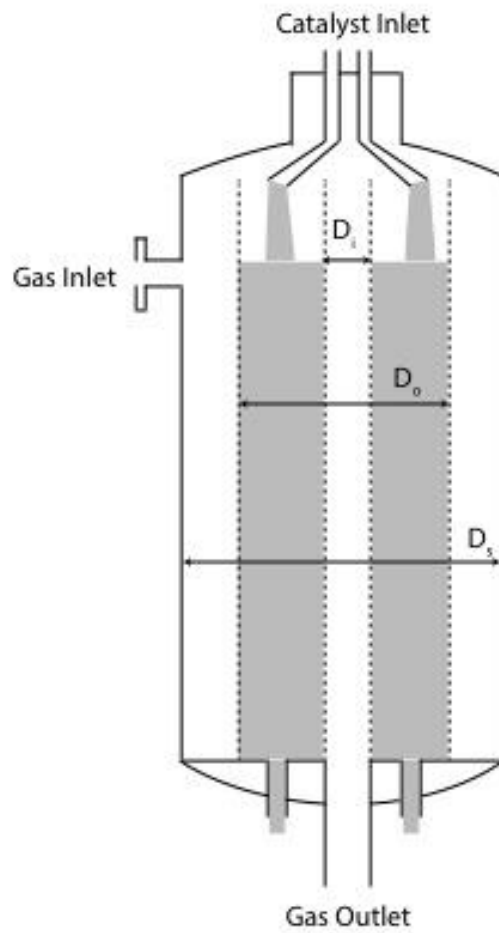
Figure 20 – Schematic representation of a reactor stage with its design parameters

Catalyst properties are tabulated in Table 11.

Table 11 – Relevant properties of the HZSM-5 catalyst

Property	Value
Bulk density (kg/m^3)	700
Particle diameter (m)	0.003
Void fraction	0.4[1]
Particle density	1,166

[1] Assumed based on common values reported in the literature

[2] Based on assumed void fraction

3.3.2 Catalyst Regeneration

The stacked reactor stages in the Cyclar process host HZSM-5 catalyst [33]. A deposit of coke forms on the catalyst [19] at a rate lower than 0.02 wt% of the feed [33]. This low deposition rate insures mild regeneration requirements and a longer catalyst life [33]. The regeneration allows a total recovery of the catalyst's selectivity and activity, and the mechanical strength and resistance of the catalyst permits continuous regeneration [33]. The regenerator is independent of the rest of the process and therefore can be run at independent conditions or be shut down momentaneously without affecting the process [19]. The major factors influencing the needed amount of catalyst and the regeneration rate are the aforementioned reaction pressure [19] and the addition of pentanes and olefins to the feedstock, as the coking rate on the catalyst is higher for the conversion of these compounds [19]. This last factor supports the design choice of a feedstock of propane and butane to the toluene plant. The catalyst flows by gravity from the top of the reactor stack to the bottom. It is then carried by lift gas such as nitrogen or other recycle gases to the catalyst regenerator and to the top of the reactor stack [18]. A detailed regeneration system is presented in Figure 21.
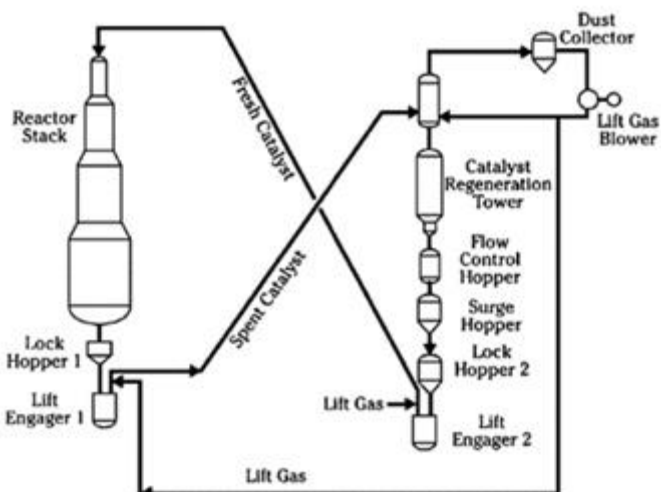
Figure 21 – Catalyst continuous regeneration system (adapted from [33])

The catalyst undergoes a series of steps inside the regeneration unit. These steps include calcination, where the coke is burnt at high temperatures (approximately 400°C), redistribution of the doping metals in the catalyst through chloride addition and drying [13].

The version of UniSim used to perform simulations does not provide tools for CCR modeling. It was assumed, for simulation purposes, that the catalyst does not coke or deactivate and implementation of the unit in the simulation was disregarded. This assumption is reasonable, since the CCR systems allows a complete regeneration of the catalyst [33].

3.4 Separation Processes

The sequence of separation was designed so that the easiest separations were done first. A flash separator was used for a preliminary separation as it is the most economical method and because the resulting separation was adequate. All subsequent separations were done in distillation units as it is the second most economical method to separate compounds, and because the separation of hydrocarbons was easily performed on the basis of difference in boiling points. Absorption towers could have been used, however it did not represent the optimal solution, as they would require further separation to remove and recover the absorbent, which would increase both the capital and operating costs. The details of the design of the separation processes are presented in this section.

3.4.1 Flash Vessel V-201

The purpose is flash vessel V-201 is to achieve a preliminary separation of the products (benzene, toluene and xylenes) from the others components present in the reactor effluent (hydrogen and C_1-C_8 hydrocarbons). The reactor effluent is cooled from 481°C to 0°C before being sent to the flash vessel. This temperature was selected from a study performed on benzene, toluene and xylenes recovery as well as the level of impurities in the bottoms of the flash vessel for a given pressure of 151 kPa, which is the pressure at the exit of heat exchanger HX-101. This study is presented in Chapter 4. It is to be noted that only 1.43 kg/h of unconverted propane is lost as a contaminant in the liquid outlet of this vessel.

In order to reach 0°C, stream 112 is cooled against stream 103, the reactor feed, in HX-101. The pressure drop across the heat exchanger is estimated to 10 kPa based on heuristics on condensing fluids in heat exchangers.

3.4.2 Distillation Column Design

The design of a distillation column is very complex, as it is comprised of multiple steps, which are all interrelated. The most important steps are the determination of the separation basis as well as the number of equilibrium stages required for this separation to occur. This step then allows for the sizing of the diameter and height of the column.

To determine the separation basis, one must look at the relative volatilities of the components in the feed stream. The most volatile components, which have a low normal boiling point, will vaporize in the column and be recovered in the distillate at a high purity. The other components will remain in the liquid phase and be recovered in the bottoms. Table 12 lists the most abundant compounds present in the system, in order of their boiling points.

Table 12 – Normal boiling points of components [1]

Component	Normal Boiling Point (°C)
Hydrogen	-252.8
Methane	-161.5
Ethane	-88.6
Propane	-42
Benzene	80.1
Toluene	110.6
Xylenes	138.5

The FUG method is a design procedure proposed by Fenske, Underwood and Gilliland. It allows for the calculation of the number of equilibrium stages required for the distillation by using a shortcut method. This shortcut method provides initial estimates for the minimum number of trays, the location of the feed tray, as well as the minimum reflux ratio.

Refer to Appendix C for a complete step-by-step design procedure of a distillation column using the FUG method.

Please note that a calculation mistake may have been made while designing the distillation columns, since they all have a very small diameter resulting in a high aspect ratio. However, due to time and staff limitations, a thorough investigation could not be performed. Nonetheless, the compounds are separated adequately based on the separation basis selected for each column.

3.4.2.1 Distillation Column T-301

This distillation column is used in order to achieve a better separation of BTX from hydrogen and light hydrocarbons coming from the gas outlet of flash vessel V-201. The temperature, pressure and location of the tower feed were selected based on a study conducted on the energy required from the reboiler and condenser. This study is presented in Chapter 4. The following Table 13 summarizes the design parameters of this column.

Table 13 – Design parameters of T-301

Design Parameter	Value
Material of Construction	Carbon Steel
Inlet Temperature (°C)	0
Inlet Pressure (kPa)	151
Number of Trays	12
Feed Location	6th Tray
Diameter (m)	0.69
Height (m)	6.4
Propane Recovery (%)	98

No benzene, toluene or xylenes exit T-301 in vapour phase; all products are therefore sent to the BTX recovery section (Section 400). The condensation is partial because the distillate stream is extremely volatile (mainly because of the hydrogen) and a total condensation would require too much energy from the condenser. The gas stream exiting the condenser is sent to the fired heater as fuel gas. The liquid stream exiting from the condenser, which contains the unconverted propane, is sent to distillation tower T-302 for propane recovery. The column bottom stream is sent to distillation tower T-401 for BTX separation.

3.4.2.2 Distillation Column T-302

This distillation is used to recover propane at the bottom of the column and recycle it to the process feed stream. The temperature, pressure and location of the tower feed were selected based on a study conducted on the energy required from the reboiler and condenser. This study is presented in Chapter 4. The following Table 14 summarizes the design parameters of this column.

Table 14 – Design parameters of T-302

Design Parameter	Value
Material of Construction	Carbon Steel
Inlet Temperature (°C)	-127.9
Inlet Pressure (kPa)	120
Number of Trays	14
Feed Location	3rd Tray
Diameter (m)	0.25
Height (m)	6.7
Ethane Recovery (%)	99

The bottoms of the tower are composed of 73% propane, 14% butane and 13% light hydrocarbons. No higher purity was pursued for the recycle stream as the final products of the process were already of petroleum grade (95% purity). The bottoms are recycled or purged in a ratio of 9:1. The gas and liquid coming from the partial condenser of tower T-302 are sent to the fired heater as fuel gas. The condensation is partial for the same reason mentioned in the previous section on tower T-301.

3.4.2.3 Distillation Column T-401

While some toluene manufacturing procedures such as naphtha reforming require solvent extraction to recover the desired products, a simple fractionation is necessary to recover toluene from the final BTX stream [19] since the final paraffin content is low [24]. The properties of benzene, xylenes and toluene allow the separation of these compounds based on their boiling temperatures [59].

The purpose of this separation unit is to recover benzene at a high purity in order to sell it as a co-product. The mixed aromatics stream coming from V-201 and T-301 enters the tower at a temperature, pressure and feed location determined based on the results of a study on the reboiler and condenser duties presented in Chapter 4. The following Table 15 summarizes the design parameters of this column.

Table 15 – Design parameters of T-401

Design Parameter	Value
Material of Construction	Carbon Steel
Inlet Temperature (°C)	8.2
Inlet Pressure (kPa)	130
Number of Trays	21
Feed Location	11th Tray
Diameter (m)	0.39
Height (m)	9.5
Benzene Purity (%)	96.9

Benzene is recovered in the gas phase, as a distillate of 96.9 wt%. The bottoms, recovered in the liquid phase, consist of 32.8 wt% xylenes and 66.5 wt% toluene. This stream is sent to the final distillation column, T-402.

3.4.2.4 Distillation Column T-402

The last distillation column, T-402, separates the last two aromatic compounds: toluene and xylene. As for the previous towers, the operating conditions as well as the feed tray number were chosen based on the results of a study on the reboiler and condenser duties. This study is presented in Chapter 4. The following Table 16 summarizes the design parameters of this column.

Table 16 – Design parameters of T-402

Design Parameter	Value
Material of Construction	Carbon Steel
Inlet Temperature (°C)	126.2
Inlet Pressure (kPa)	131
Number of Trays	19
Feed Location	12th Tray
Diameter (m)	0.61
Height (m)	9.3
Toluene Purity (%)	98.9
Xylenes Purity (%)	98.0

CHAPTER 4
MISCELLANEOUS STUDIES
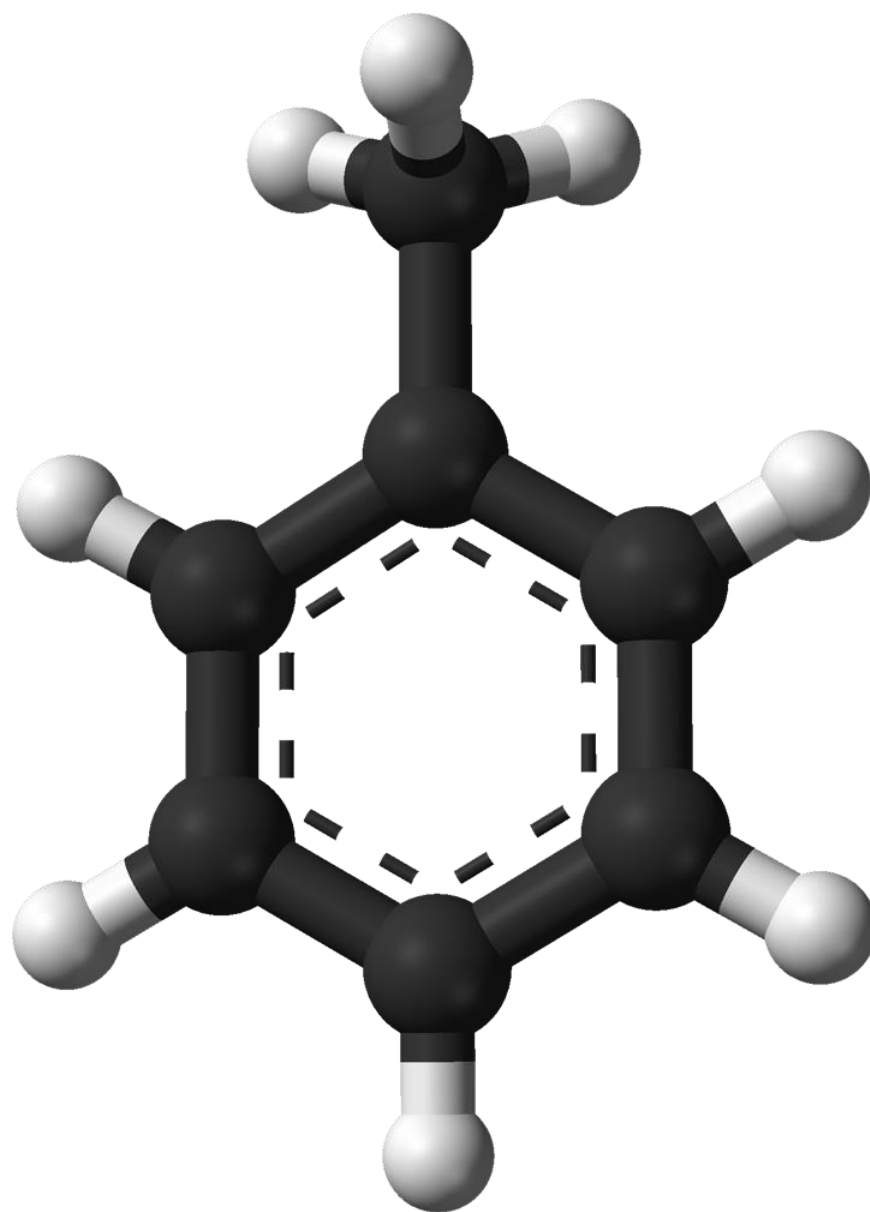
4.1 Optimization of Equipment

Once the plant is simulated for given operating conditions based on literature and on heuristics, it is possible to tune these conditions is order to yield better results and lower the operating and capital requirements. This section is dedicated to major studies conducted on pieces of equipment.

4.1.1 Flash Vessel V-201

The separation in a flash vessel depends on the pressure and the temperature in the unit; for a given pressure, a mixture will flash differently depending on the temperature. A study was conducted on the temperature at the inlet of flash vessel V-201. Temperature was chosen over pressure for this study as a heat exchanger was already required upstream to the vessel and a change in temperature therefore did not need the implementation of a new unit such as a pump or a compressor.

Temperature was varied from -3°C to 57°C. The lower bound of this interval was determined by a minimal temperature approach of 10°C in heat exchanger HX-101. The higher bound was set arbitrarily; it is however high enough to have a good understanding of the impact of temperature on the separation. The aromatics recovery for the aforementioned range of temperatures is presented in Figure 22 and Figure 23.
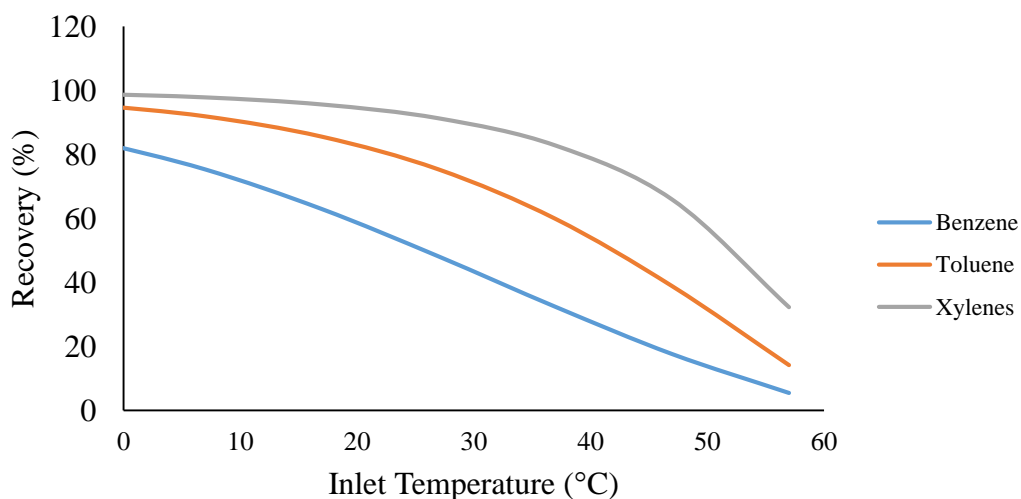
Figure 22 – Effect of inlet temperature variations on flash vessel V-201 BTX recovery
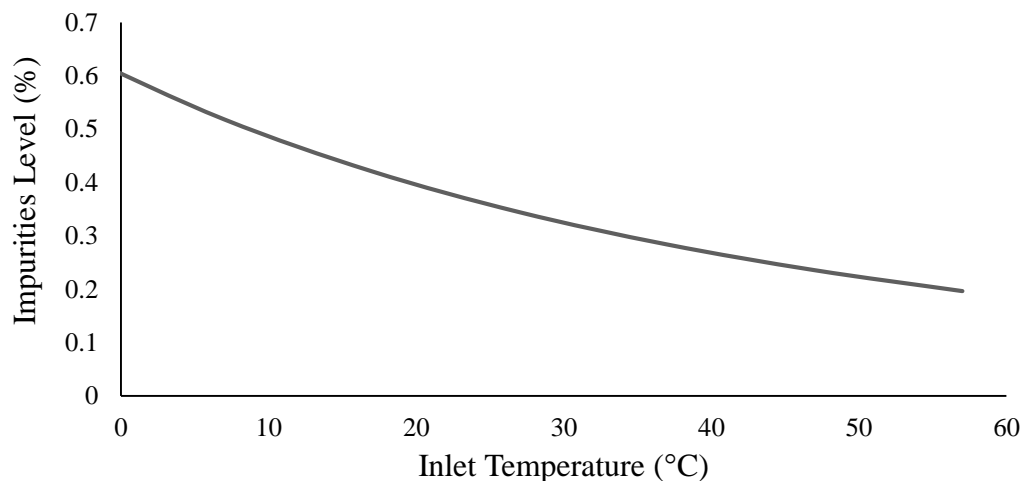
Figure 23 – Effect of temperature variations on stream 203 impurities

As can be observed from Figure 22, the BTX recovery is better at lower temperatures. However, as seen in Figure 23, the impurities level is lower at higher temperatures, as the impurities vaporize and exit through the top of the vessel. Nevertheless, the impurities level is always lower than 1%. The BTX recovery is fairly constant between -13°C and 0°C and, as there are no other units downstream dedicated to the purification of the BTX stream, a temperature of 0°C, instead of -13°C, is chosen as an intermediate to maximize the BTX recovery while lowering the impurities level.

4.1.2 Distillation Tower T-301

It was found that the final products obtained from the base case plant simulation were of petroleum grade purity (i.e. ≥ 95%). Therefore, the approach to the optimization of the towers was to lower the utilities requirements. As the simulated distillation tower T-301 is extremely sensitive to pressure changes, a single study on the feed location was conducted on this tower. No temperature study was conducted because of the requirement to add a heat exchanger upstream to the column, therefore nullifying the attempt to lower the capital and operating costs. The effect of the feed location on the total energy required from utilities for tower T-301 is presented in Figure 24.
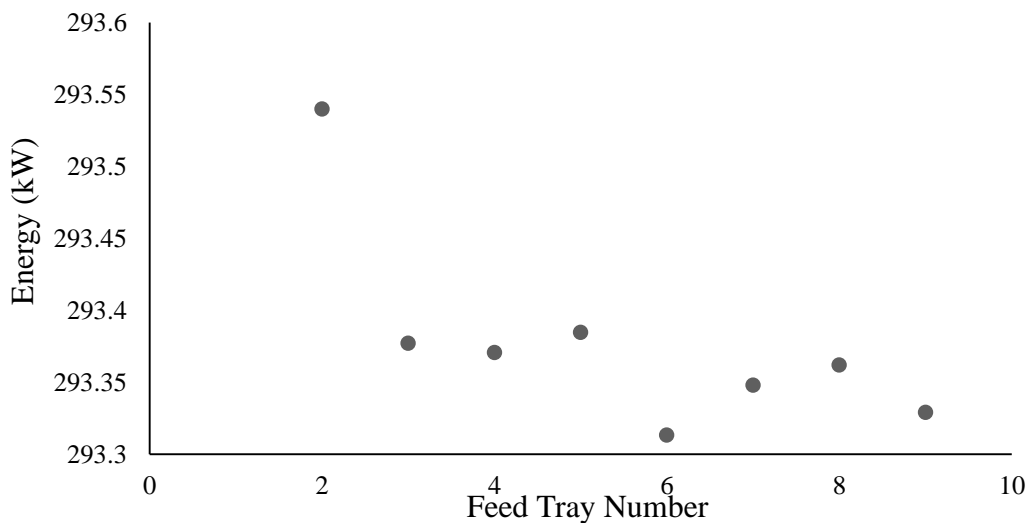
Figure 24 – T-301 Total energy required from utilities

The maximal feed tray number was 9 in order to keep the tray pressure under the feed pressure. The minimal energy requirements are met when the feed enters the tower at tray 6.

4.1.3 Distillation Tower T-302

A study on the feed location was conducted on distillation tower T-302. No feed pressure study was conducted as the feed was already near the lowest allowable feed pressure to enter the tower above the trays pressures. While a new unit could have been implanted to increase the pressure of the inlet stream, this would have contradicted the attempt to lower the capital and operating costs. The same reasoning is applicable to a temperature study. The effect of the feed location on the total energy required from utilities for tower T-302 is presented in Figure 25.
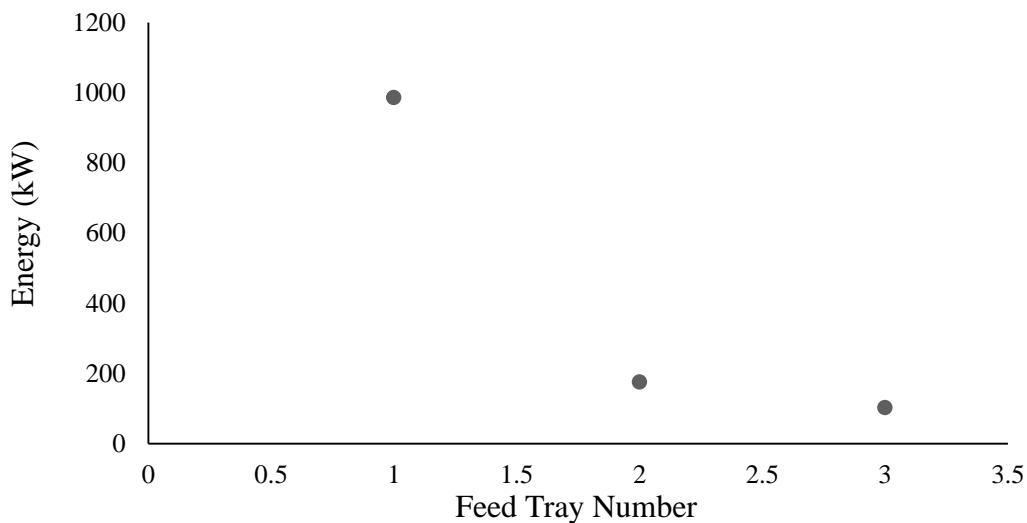
Figure 25 – T-302 Total Energy Required from Utilities

The maximal feed tray number was 3 in order to keep the tray pressure under the feed pressure. The minimal energy requirements are met when the feed enters the tower at tray 3.

4.1.4 Distillation Tower T-401

A study on the feed location was conducted on distillation tower T-401 for pressures in the range of 120-150 kPa. The highest bound of the pressure range is based on the pressure of the bottoms of tower T-302. While a compressor could have been implanted to increase the pressure of the inlet stream, this would have contradicted the attempt to lower the capital and operating costs. The pressure drop is applied by valve VL-401 upstream of T-401. The energy required on the optimal feed location for a variety of pressure in the pressure range are presented in Figure 26.
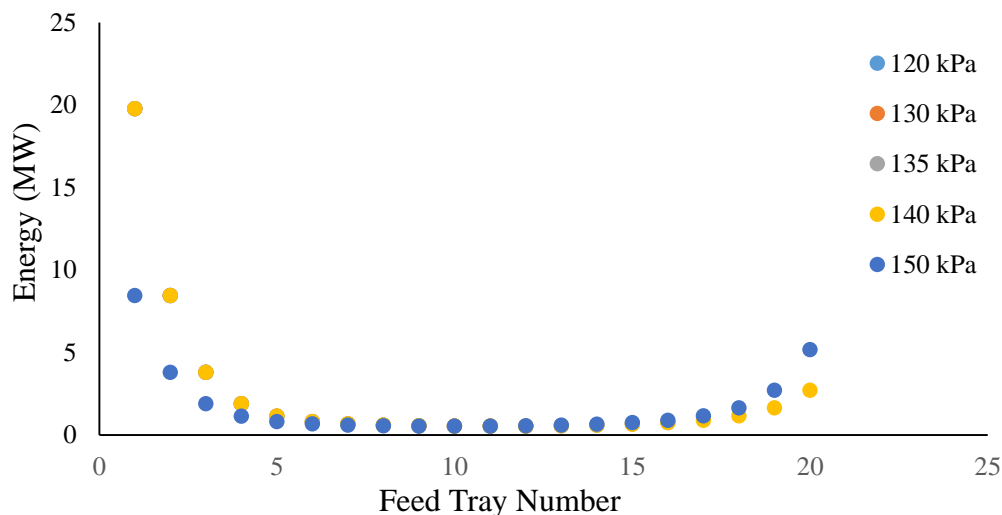
Figure 26 – T-401 Total energy required from utilities for inlet pressures of 120-150 kPa

As can been seen on Figure 26, for each pressure on the pressure range, the same utility requirements can be observed for most feed locations. The optimal feed location is on tray 11 and the total energy required from the utilities is 548 kW. A minimal pressure of 130 kPa, which is just above the tray pressure, is chosen as the operating pressure in order to lower the capital cost of the tower.

4.1.5   Distillation Tower T-402

A study on the feed location was conducted on distillation tower T-402 for pressures in the range of 130-150 kPa. The highest bound of the pressure range is based on the pressure of the bottoms of tower T-401. While a compressor could have been implanted to increase the pressure of the inlet stream, this would have contradicted the attempt to lower the capital and operating costs. The pressure drop is applied by valve VL-402 upstream of T-402. The energy required on the optimal feed location for a variety of pressure in the pressure range are presented in Figure 27.
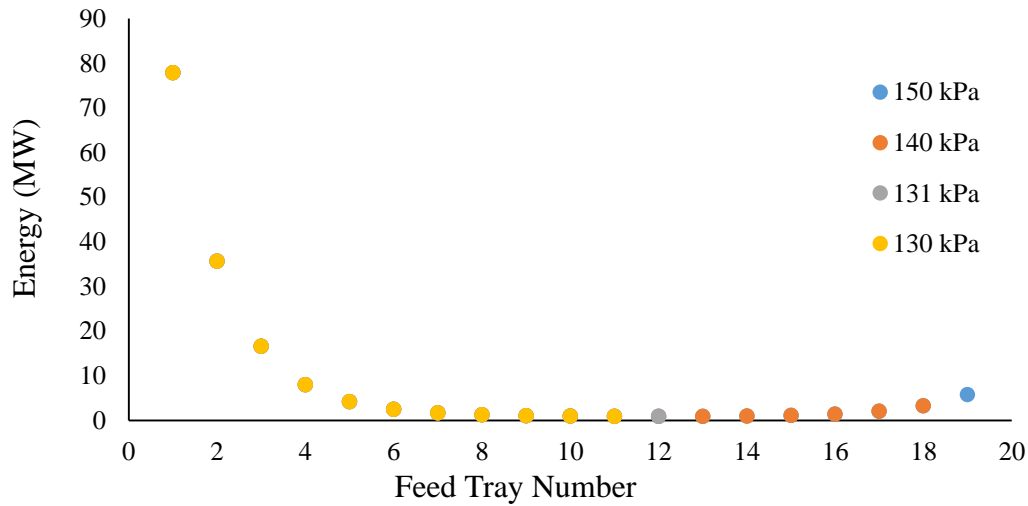
Figure 27 – T-402 Total Energy Requires from Utilities for Inlet Pressures of 130-150 kPa

As can been seen in Figure 27, for each pressure on the pressure range, the same utility requirements can be observed for most feed locations. The optimal feed location is on tray 12 and the total energy required from the utilities is 899 kW. A minimal pressure of 131 kPa, which is just above the tray pressure, is chosen as the operating pressure in order to lower the capital cost of the tower.

4.2 Heat Integration

In order to lower the utilities requirements of the plant, and therefore the operating costs, energy can be transferred between process streams. This section is dedicated to the analysis of the energy available in the process and to the design of a heat exchanger network.

The list of the process streams that are to be either cooled or heated are presented in Table 17 along with relevant characteristics. They are divided in subsections (a,b) for phase change as the heat capacity differs from liquid phase to gas phase.

Table 17 – Process Hot and Cold Streams

Stream	Phase change	Mass flow (kg/h)	Initial temperature (°C)	Final temperature (°C)	Heat Capacity (kJ/kg °C)	Energy (kW)
Hot Stream						
112a	-	4470	480.9	62.8	2.75	1431.2
112b	Condensation	4470	62.8	0	4.92	383.9
Cold Stream						
103a	Evaporation	4482	-13.5	-9.4	74.4	378.4
103b	-	4482	-9.4	550	2.66	1852.5

4.2.1 First Heat Exchangers Network Design

A minimal temperature approach of 10°C is used in the heat exchangers network. Figure 28 shows the available energy to transfer between process streams for some temperature interval; these intervals are determined from the initial and final temperatures of the cold and hot streams.
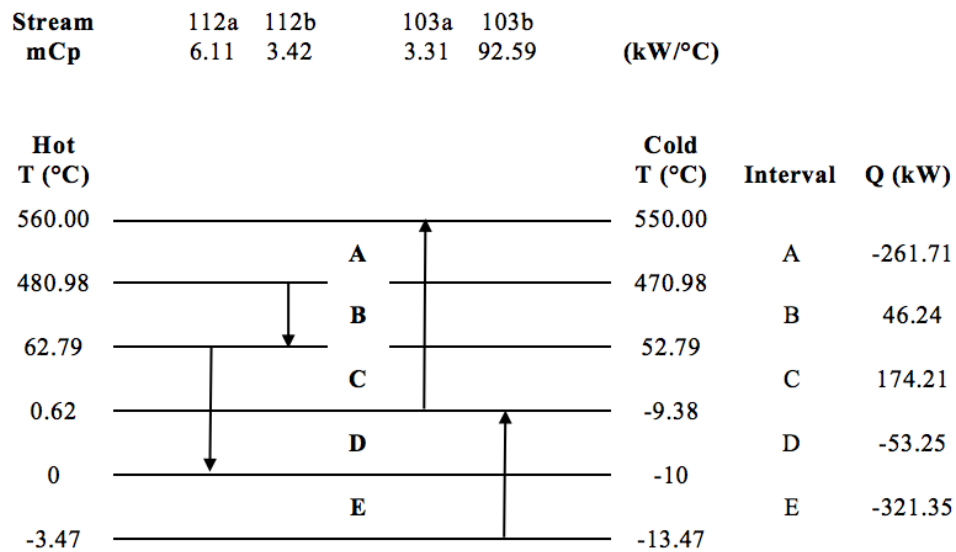
Figure 28 – Temperature interval diagram for heat exchangers network design #1

66

The excess energy from each temperature interval can be transferred to the next, from the top to the bottom of the temperature interval diagram. In the event that a negative quantity of energy is encountered, heat from outside heat sources, such as steam or a fired heater, must be added to the system. A cascading diagram of the energy transferred from one temperature interval to the next is presented in Figure 29.
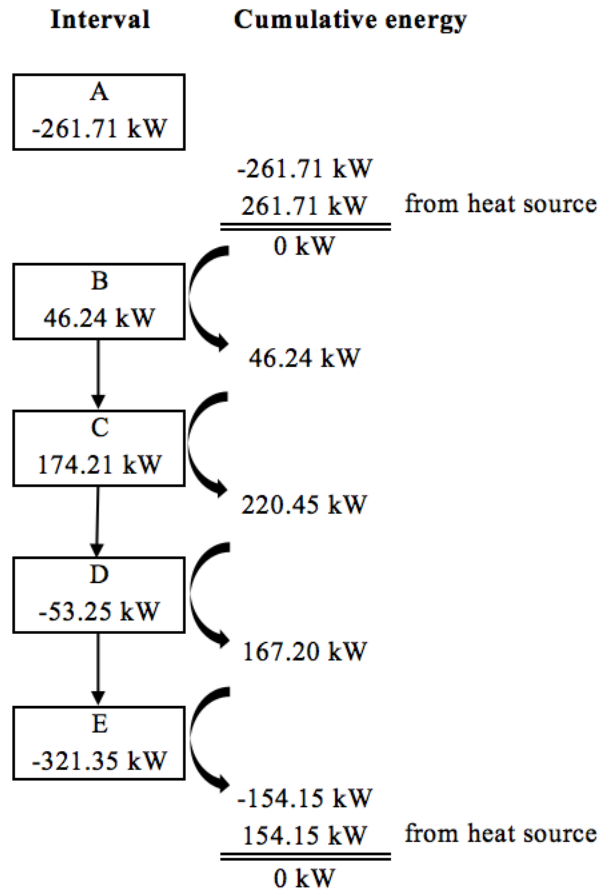
Figure 29 – Energy transfer from temperature intervals for heat exchangers design #1

As can be observed from Figure 29, two pinches are found in the system. The first pinch occurs when cold stream 103 is heated to a maximal temperature of 470.98°C by hot stream 112 as a result of the minimal temperature approach of 10°C. A fired heater would have to add 261.71 kW to stream 103 to bring it to its final temperature of 550°C. The second pinch appears when the hot stream 112 has given all its energy to cold stream 103 and reach its final temperature of 0°C. The minimal temperature of the cold stream at the inlet of the heat exchanger is then -11.83°C. There is a 154.15 kW left that should be transferred by utilities to cold stream 103

before its entrance to the heat exchanger in order to heat it from its initial temperature of -13.47°C to -11.83°C. The heat exchanger network is presented in Figure 30.
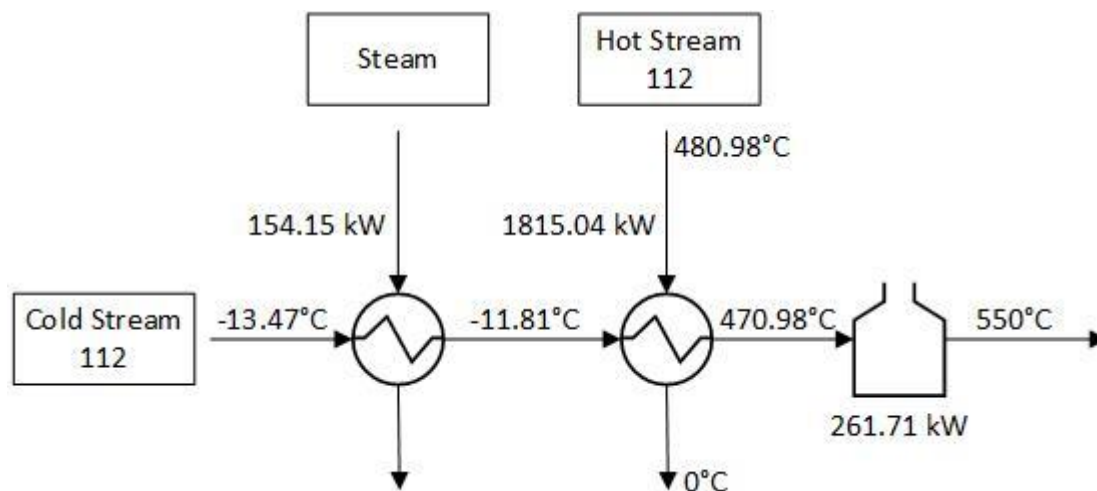
Figure 30 – Heat exchanger network design #1

This configuration is not optimal as it would be more convenient to supply all the required heat to cold stream 103 from a fired heater at the exit of the heat exchanger, removing steam utilities, as fuel gas is available in large quantities from the co-products and by-products produced in the plant. This would require the cold stream to be heated from -13.47°C to a temperature lower than 470.98°C. A second design is presented in the following section.

4.2.2 Second Heat Exchangers Network Design

With the help of UniSim, it was possible to determine the maximal temperature that cold stream 103 could reach against hot stream 112 if entering the counter-current heat exchanger at -13.47°C. This temperature is of 453.04°C. The details of the available energy to transfer between process streams for various temperature intervals is presented in Figure 31.
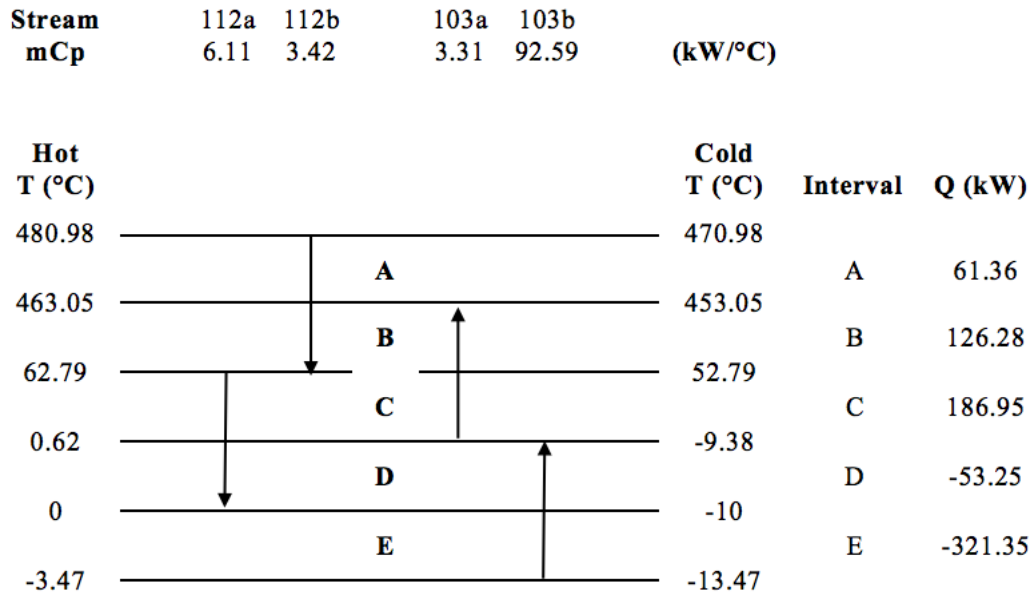
Figure 31 – Temperature interval diagram for heat exchangers network design #2

A cascading diagram of the energy transferred from one temperature interval to the next is presented in Figure 32
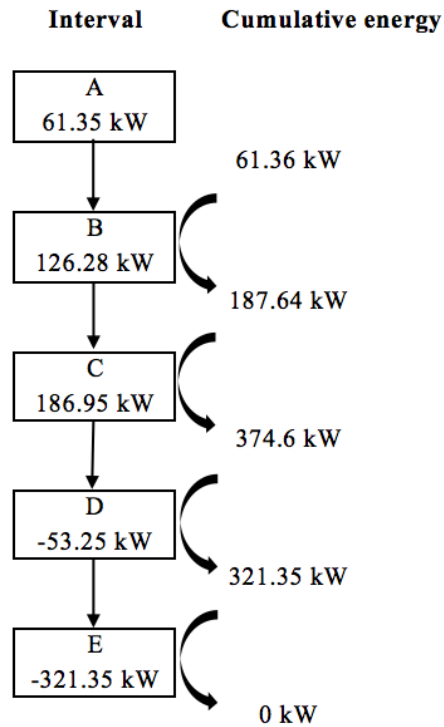
Figure 32 – Energy transfer from temperature intervals for heat exchangers design #2

This design is more convenient as there is no pinch in the system, and therefore additional utilities are not required. The hot stream is cooled to its final temperature of 0°C, while the cool stream is heated from its initial temperature of -13.49°C to a maximal temperature of 453.05°C before being sent to a fired heater to reach the reactor temperature. The heat exchanger network is presented in Figure 33.
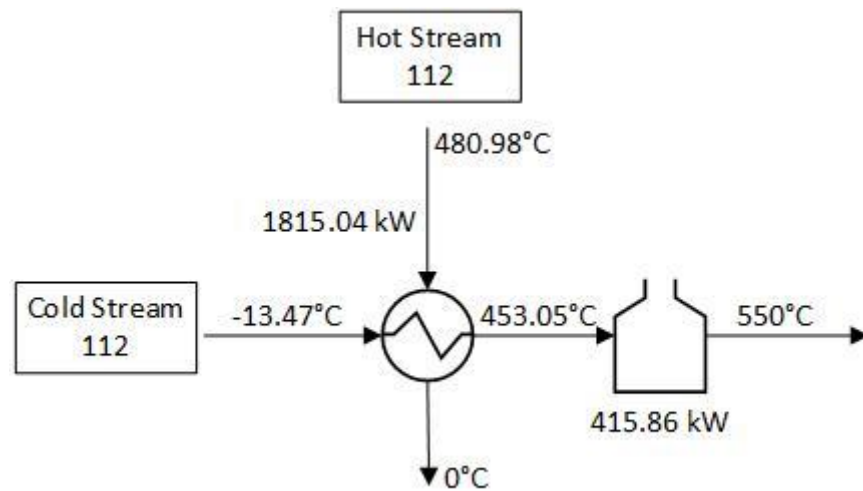
Figure 33 – Heat exchanger network design #2

The minimal temperature approach of 10°C is respected through the heat exchanger as can be observed on the temperature-enthalpy diagram presented in Figure 34.
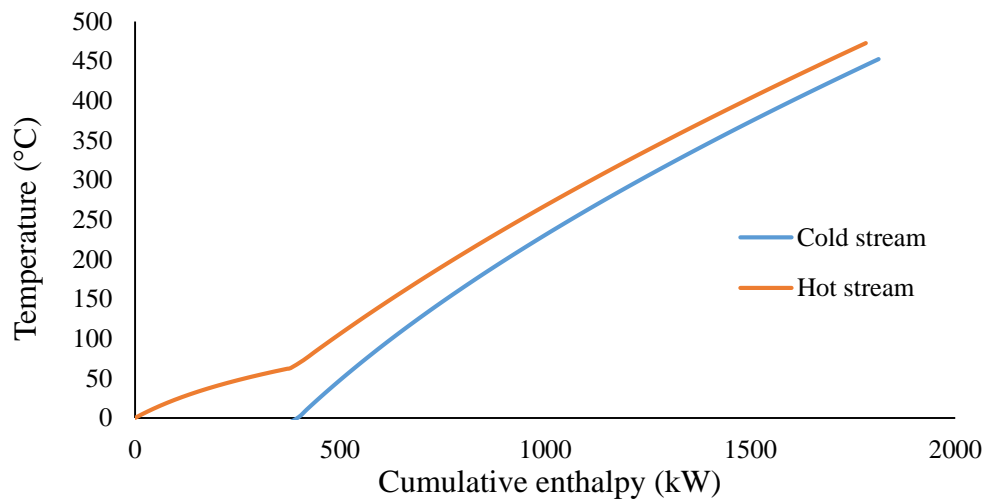
Figure 34 – Temperature-enthalpy diagram for HX-101

4.3 Start-Up Philosophy

The plant start-up and shutdown should be addressed thoroughly for economical and safety reasons. In all cases, safety is the first priority. It goes without saying that the commissioning and decommissioning of a plant will involve a specific set of protocols and procedures, because the process will operate at transient state. These procedures will also apply when production stops momentarily for maintenance purposes such as catalyst replacement, cleaning of equipment or for troubleshooting major issues.

Start-up and shutdown procedures in this plant are expected to be carried out on an annual basis, under the assumption that the plant will operate 50 out of 52 weeks and that the days where the plant is not operating are consecutive.

Given that some of the personnel, including operators, may not have a deep understanding of the chemical process, having clearly written standard operating procedures is essential to allow for an optimal transition from transient to steady-state operations.

4.3.1 Start-up Considerations

The initial start-up of a plant is a critical milestone in the venture. Carefully following a set of safety procedures can significantly reduce the risk of catastrophic unforeseen events during start-up. Bahadori provides an excellent overview of the procedures that should be employed prior to the initial plant start-up [60]. An overview of the steps is summarized.

First, an "operational check-out" should be performed to make. The flowsheet should be followed line by line and all elements included on the flowsheet should be located in the plant. It is of prime importance that all pieces of of equipment such as valves, control valves, and gate valves be properly installed and have the proper orientation. Failure to install this equipment properly could result in reverse flow or flow blockage. All connections, purges, bypass lines, drains, bleeders should all be correctly installed and positioned. Finally, pumps, compressors, heaters and other important units should be inspected to ensure they are ready to be operated.

Hydrostatic testing should be performed. This step is also key in preventing accidents, as it allows to identify faulty equipment. Introducing a liquid in the equipment may reveal whether the equipment material of construction is strong enough and whether the welding is well done.

For LPG plants, oil is recommended. Of course, the material should be drained properly after the test prior to being dried. All gaskets, joints and flanges should be tested for leakage.

The equipment should be inspected visually in order to make sure that all removable parts such as trays, catalyst support screens (reactor), level instruments are properly installed. Furthermore, equipment such as pumps should be given a preliminary run in order to ensure they provide a sufficient pressure increase and that they function properly.

All the instrumentation such as control valves, mass flow controllers or manometers should be properly installed, calibrated and they should be in working order.

The reactor and the fired heaters are potentially hazardous pieces of equipment. An important step to consider with respect to the catalytic reactor is the removal of oxygen which may affect the reaction system. This can be achieved by creating a vacuum in the reactor, or by introducing inert nitrogen in the system until the nitrogen purged is low in oxygen (< 100 ppm). With respect to the fired heaters, it is crucial to make sure that the firebox is steamed out to purge the gas that may have accumulated and prevent sudden flame formation.

4.3.2 Shutdown Considerations

It is equally as important that adequate shutdown procedures be implemented. For example, all flammable streams should be redirected to a flare prior to shutting down the plant. All lines and vessels should be purged from any remaining hydrocarbons and washed prior to plant shutdown for example. Running a non-flammable liquid through the circuit may displace the dangerous hydrocarbon.

CHAPTER 5
OUTSIDE BATTERY LIMIT
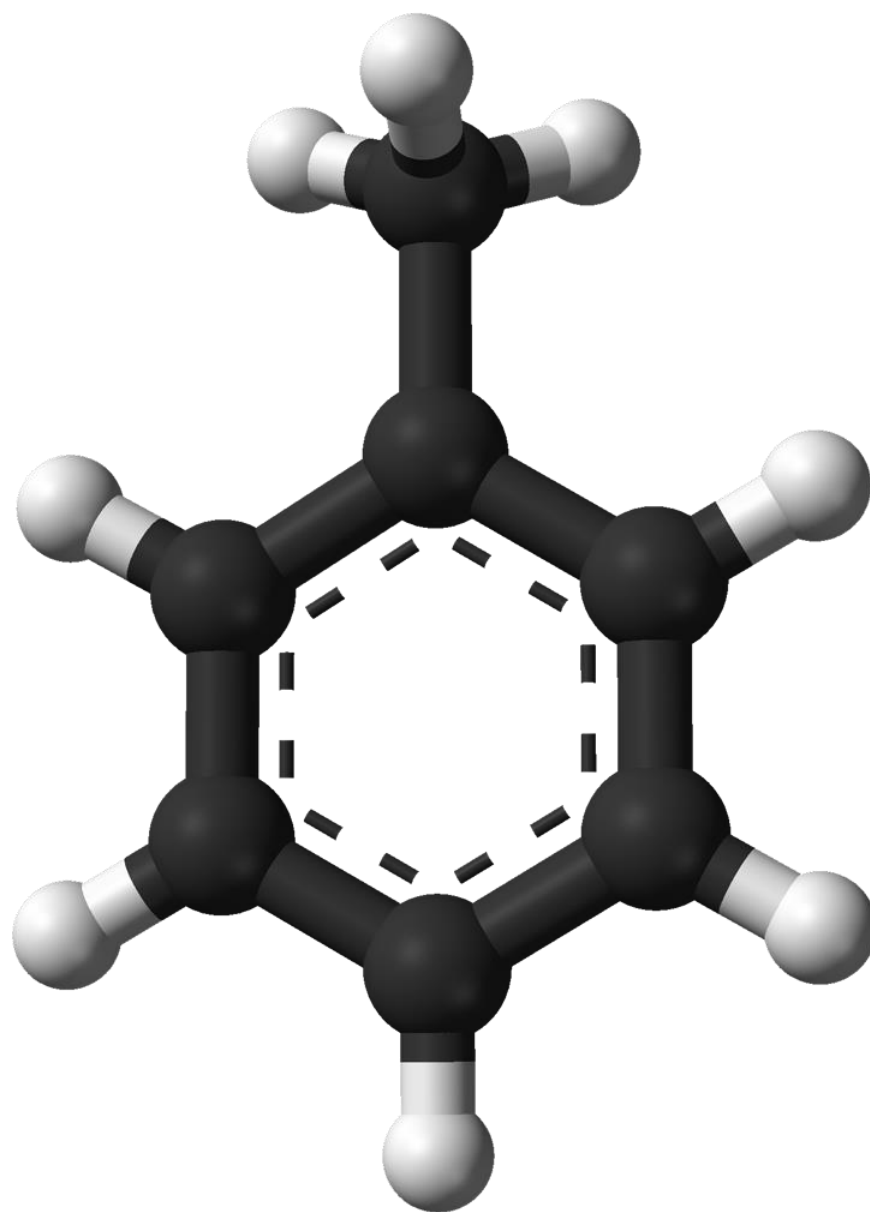
5.1 Plant Layout

Much consideration must be given to the spatial arrangement of the plant and to the positioning of the various unit operations and storage equipment. Carefully designing the plant layout can have a significant impact on process economics and safety as well as on maintenance or logistics [61].

Finding the adequate distance between units and other components in the plant can be challenging, as a compromise must be made between pressure drop and safety. Lower distances between units yield lower pressure drops, as fluids travel smaller distances through pipes. This results in savings through operating cost cuts, as the duty of the pumps and/or compressors is decreased. However, units and other equipment should not be so close as to make them difficult to access [62]. It is reasonably foreseeable that equipment will need to be cleaned, inspected and repaired, therefore, it is important to allocate enough room to facilitate these tasks [61]. Insufficient distance between unit operations and/or storage vessels can pose significant risks, particularly so in plants comprising flammable, explosive or toxic materials. It was mentioned previously that safety concerns should be prioritized over economic considerations, and that all possible measures possible should be taken to mitigate the risks to human life, the environment and economic interests.

A rational assessment of requirements can dictate where sections and elements of the plant should be positioned relative to each other. For example, it is only logical that hazardous unit operations should be kept as far as possible from other hazardous units or office spaces for example.

Figure 35 represents an aerial view of the plant, which is described in more details in Sections 5.1.1 and 5.1.2

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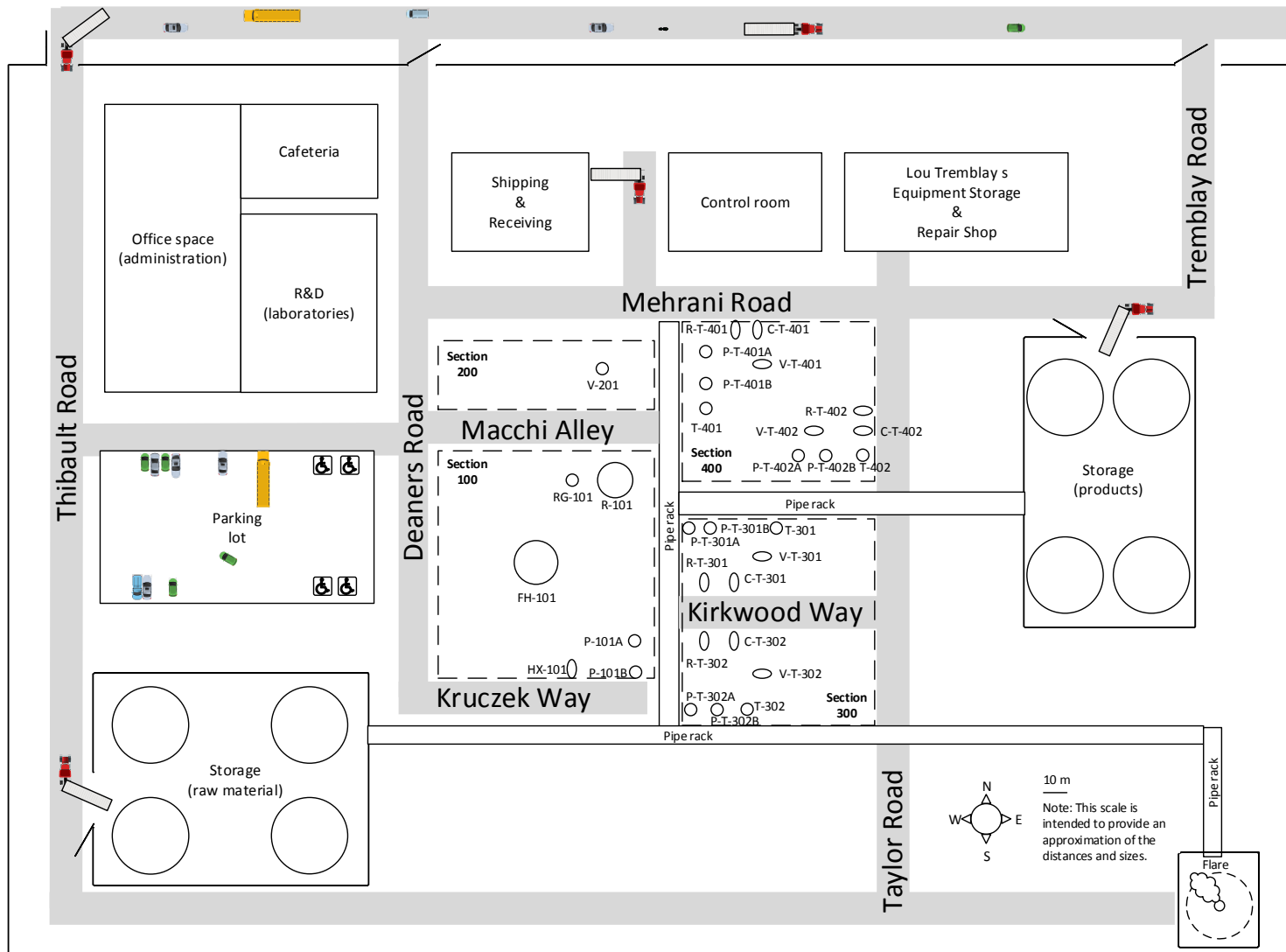
Figure 35 – Plant layout

5.1.1 Inside Battery Limit

Sections 100, 200, 300 and 400 of the plant are all considered to be inside battery limit.

The units in Section 100 are quite far apart from one another. The fired heater (FH-101) warrants the large distance between the units, as explosion hazards are associated with the operation of a fired heater. Ideally, the fired heater should have been better isolated due to the dangers of gas propagation via the wind following a possible leak. Less hazardous units such as the heat exchanger (HX-101) and the recycle pumps (P-101A/B) are closer to the pipe rack, because they are less likely to cause damage in the eventuality that they fail. The FH-101 and the reactor (R-101/RG-101) can easily be accessed via Macchi Alley and Kruczek Way.

Sections 300 and 400 differ mainly in their purpose. Section 300 was designed to recover the light ends, whereas Section 400 aims to separate the aromatics. It is logical that Section 400 should be located close to the farm tank for the products and Section 300 should be located close to both Section 100, which encloses the recycle pump and the fired heater, and to the flare. The accessibility of the heat exchangers was favoured over that of the pumps and vessels, as one can anticipate that the heat exchanger tubes will need to be cleaned and or changed. Mehrani Rd. and Kirkwood Way allow for easy access to these units.

The portion south of Sections 100 and 300 was left empty on purpose to facilitate eventual plant expansion projects [62].

5.1.2 Outside Battery Limit

The layout of the elements of the plant outside the battery limit in this particular case is as important as the layout of the process units, since highly flammable materials are stored and flared. The tank farms and the flare pose significant risk for obvious reasons and their position should be thoroughly assessed.

The raw material and product tank farms are located at the West and East ends of the plant. This reduces the extent of the damage that would occur if an explosion occurred in one of the tank farms. Particular care was taken to position these nodes as far away as human activity as possible. The raw material tank farm is separated from the office space and laboratories by a parking lot while the product tank farm, although slightly closer to the repair shop, is far from

most other buildings. Administrative buildings and other facilities separate the process from the main road.

Space was allotted between the flare stack and the rest of the plant. The ISO23251 standard provides recommendations regarding the design of flare stacks, but in-depth calculations could not be carried out due to time limitations [63].

Office space, laboratories and shipping & receiving are located next to the main road in order to spare the non-operators and non-technical staff the unnecessary travel of through the plant.

5.2 Utilities

Multiple utilities are necessary for the good operation of the plant. While heat integration presented in Chapter 4 allowed to reduce the amount of utilities needed to heat or cool down process streams between major units, high and low pressure steam, cooling water, liquid nitrogen refrigerant and electricity are still required for the operation of the units themselves. This section is dedicated to the mass balances of utilities around relevant units and around the overall plant.

5.2.1 Steam Balance

The amount of steam needed through the plant are presented in Table 18 and

Table 19. All the steam is used in the distillation towers reboilers. The total amount of steam required for the operation of the plant is 1,035 kg/h for LPS and 10,421.97 kg/h for HPS.

Table 18 – Plant LPS requirements

Unit	Temperature (°C)	Pressure (kPa)	Mass flow (kg/h)
T-301 Reboiler	134.4	308.2	217.90
T-302 Reboiler	134.4	308.2	817.74
		Total LPS	1,035.64

Table 19 – Plant HPS requirements

Unit	Temperature (°C)	Pressure (kPa)	Mass flow (kg/h)
T-401 Reboiler	251.3	4000	5,255.55
T-402 Reboiler	251.3	4000	5,166.42
		Total HPS	10,421.97

5.2.2 Liquid Nitrogen Balance

The amount of liquid nitrogen required for the plant is presented in Table 20. Liquid nitrogen is required in the condenser of distillation columns T-301, T-302 and T-401. The total amount of liquid nitrogen required for the operation of the plant is 6,604.5 kg/h.

Table 20 – Plant liquid nitrogen requirements

Unit	Temperature (°C)	Pressure (kPa)	Mass flow (kg/h)
T-301 Condenser	-196 to -122	101.3-86.3	3,747
T-302 Condenser	-196 to -100	101.3-86.3	266.5
T-401 Condenser	-196 to -73	101.3-86.3	2,591
		Total liquid nitrogen	6,604.5

5.2.2 Cooling Water Balance

The amount of cooling water required for the plant is presented in Table 21. The only cooling water stream needed is for distillation tower T-402 condenser, as all other condensers require refrigerant. The total amount of cooling water required for the operation of the plant is 68,554.51 kg/h.

Table 21 – Plant cooling water requirements

Unit	Temperature (°C)	Pressure (kPa)	Mass flow (kg/h)
T-402 Condenser	20-50	116.3-101-3	68,554.51
		Total cooling water	68,554.51

5.2.3 Fuel Balance

The amount of fuel gas required for the plant is presented in Table 22. All the fuel gas is combusted in the fired heater FH-101 for feed preparation and reactor inter-stage heating. The total amount of fuel required for the operation of the plant is 910.4 kg/h. This amount was calculated from the heat required by the fired heaters and the heat produced by the combustion of the fuel gas. This fuel gas is obtained from the mixing the methane/ethane rich streams coming from distillation towers T-301 and T-302 with the propane purge stream. It was assumed that a conversion of 80% would occur for the combustion of the fuel gas when combined with a stoichiometric amount of ambient air, which is of 42,502.83 kg/h.

Table 22 – Plant fuel gas requirements

Unit	Temperature (°C)	Pressure (kPa)	Mass flow (kg/h)
FH-101	-121.6	101.3	910.4
		Total fuel gas	910.4

5.2.4 Power Balance

Power is required to supply pump P-101 as well as the reflux pump of each of the plant distillation towers. The amount of power required for the entire plant is presented in Table 23. The total amount of power required is 4,435 W. The amount of electricity required for the pumps is very small. This can be due to the fact that the estimated velocity in the pipes when designing

the pumps is very small because the flow rates are fairly small as well, or due to assumptions made while sizing the pumps with Bernoulli's principle.

Table 23 – Plant power requirements

Unit	P-101	T-301 Reflux Pump	T-302 Reflux Pump	T-401 Reflux Pump	T-402 Reflux Pump	Total power
Power (W)	890	532	113	542	2,367	4,435

5.3 Waste Balance

The toluene plant produces three product streams, which are benzene, toluene and xylenes at petroleum grade. There are four other process streams leaving the plant. These are labelled as streams 301, 304, 305 and 308 on PFD 300 presented in Chapter 2. Process streams 301, 304 and 305 are mainly composed of hydrogen, methane and ethane while process stream 308 is the propane purge. These four streams may be combined into a 2221 kg/h stream and be partially used as fuel gas for the plant fired heater. The amount of fuel gas needed is 910.4 kg/h, as exposed in section 5.2.4. It is combined with air for combustion to occur. The exit stream of the fired heater is mostly composed of oxygen, nitrogen, water and carbon dioxide, for a flow rate of 43,413 kg/h. Table 24 presents the waste balance for the plant. The waste streams are sent to hazardous waste treatment.

Table 24 – Plant waste balance

Waste	Composition	Mass flow (kg/h)
Fired heater fuel outlet	75% N_2 - 14% O_2 - 7% H_2O - 3% CO_2	43,413.0
Excess fuel gas	54% CH_4 - 34% H_2 - 10% C_2H_6 - 2% C_2H_4	1,310.6
	Total waste	44,723.9

CHAPTER 6
ENVIRONMENTAL AND SAFETY CONSIDERATIONS

6.1 Component Characteristics

For this process, propane is the only raw material used to produce toluene. The main products produced along with toluene are: hydrogen, methane, ethane, benzene and xylene. However, many other hydrocarbons and aromatics are produced during the reaction, but are typically found in trace amounts. The following Table 25 presents the characteristics of the main components; the information was taken from the complete material safety data sheets (MSDS), which are available in Appendix I. All of these compounds are flammable.

Table 25 – Main components characteristics

Common Names	Chemical Formula	Molar Mass (g/mol)	Appearance	Normal Boiling Point	Auto-Ignition Temperature
Hydrogen	H_2	2.02	Colourless, odourless gas at normal temperature and pressure	- 252.8°C	565.5°C
Methane	CH_4	16.0	Colourless, odourless and flammable gas	- 161.5°C	537°C
Ethane	C_2H_6	30.1	Colourless, odourless gas	- 88.6°C	515°C
Propane	C_3H_8	44.1	Colourless liquid and vapour when stored under pressure	- 42°C	432°C
Benzene	C_6H_6	78.1	Colourless liquid with strong aromatic odour	80.1°C	497.78°C
Toluene (Toluol, Methylbenzene)	C_7H_8	92.1	Clear colourless liquid with sweet smell	110.6°C	480°C
Xylene (Dimethylbenzene, Methyltoluene)	C_8H_{10}	106	Clear colourless liquid with sweet smell	138.5°C	464°C

6.2   Key Safety Issues

The main safety issues related to toluene synthesis arise mainly from the process operating conditions as well as the properties of the compounds. The system operates at high temperatures and pressures above atmospheric conditions. Consequently, additional care should be taken and the process control of the system needs to be accurate to avoid any unpredicted accidents within the system.

Toluene is a volatile organic compound and therefore can be classified as a primary pollutant [64]. Additionally, toluene is flammable and should consequently be used and stored in a cool, dry, well-ventilated areas and should not be used where fire hazards may occur or close to easily sparking materials (refer to Appendix I).

Toluene can cause harm to the human body, as it is moderately toxic if ingested or inhaled and slightly hazardous if absorbed through the skin [64]. Moreover, toluene acts as a central nervous system depressant, and can present effects for both acute and chronic exposures. Some of the symptoms include depression, loss of memory, as well as progressive brain and nerve damage [64]. The exposure limit is typically 50 ppm TWA. It has been concluded that toluene can cause more harm to humans than it can for fish and wildlife. This is mainly due to its high volatility; toluene is usually evaporated into the atmosphere before being absorbed in water and/or soil [64].

6.2.1   Reactor Safety Features

Although the reaction system is globally endothermic, preventing the risks of runaway reactions, operating the RFMBR reactor is associated with some reasonably foreseeable hazards.

6.2.1.1   Leak Hazard

One must consider the possibility that a leak may occur as a result of prolonged operation or physical damage caused by a worker. Many of the components in the reaction system are flammable and/or toxic for humans, therefore it is important to ensure that outer shell of the reactor is properly coated or isolated to redirect the flow of leaked gas to a flaring system for example.

6.2.1.2 Pressure Hazard

Some sort of blockage may cause the pressure to rise inside the reactor, so it is important that a proper pressure control system be implemented. For instance, a fail-to-open valve could redirect the flow of gas to a flare in order to prevent pressure build-up inside the reactor.

6.2.1.3 Accessibility

Precautions must be taken such that access to the reactor is limited to individuals with the relevant capacity (trained operators and engineers). Work done around the reactor should be done carefully in order to prevent damages to the reactor or burns.

6.2.2 Heat Exchanger Safety Features

Heat exchangers require hazard evaluation and safety measures. They operate at very high temperatures and pressures. A list of possible hazards around heat exchangers is presented in this section.

6.2.2.1 Temperature Hazard

Heat exchangers operate at high temperatures. The piping and the heat exchanger itself are be labeled as dangerous to prevent skin burn. They are isolated in order to prevent heat losses and burns.

6.2.2.2 Leak Hazard

The feed of the process, propane, is a well-known combustible. The same situation applies to most compounds created in the plant. A well-designed process should avoid any ignition sources around the heat exchanger in case of leaks. Fire control devices should be available on the plant. A fire escape plan should be implemented.

6.2.2.3 Temperature and Pressure Build-up

In the case of a valve malfunction, pressure and temperature could build-up in the heat exchanger. Temperature and pressure alarms should be implemented as well as pressure release valves.

6.2.3 Distillation Towers Safety Features

There are few possible hazards associated to the operation of distillation columns since pressure and temperature changes occur.

6.2.3.1 Temperature Hazard

The towers typically operate at high temperatures in order to vaporize the most volatile components according to their boiling points. Therefore, the component mixture is hot and can damage equipment if the proper material of construction is not selected. Adequate control loops should be implemented around the condenser and reboiler. The temperature of the distillate and bottoms streams should be controlled by the flow of cooling fluid and steam going into the heat exchangers, respectively.

6.2.3.2 Pressure Hazard

The towers may operate above atmospheric pressure. If the wall thickness of the vessel is too thin such that it cannot sustain the exerted forces, or if the pressure increases without control, the vessel may explode. To prevent this pressure build-up from happening, the pressure in the tower must be controlled by the gas outlet flow rate with a fail-to-open control valve. Moreover, a pressure relief valve should be added in order to purge the excess gas and flare it, in the case of an emergency.

6.2.3.3 Leak Hazard

The chemicals used in the process are highly flammable and moderately toxic to humans, animals and the environment. If there were to be a leak, the mixture of organic aromatic hydrocarbons may ignite and cause a fire or an explosion. For the safety of operators and nearby communities, the process equipment should be properly coated to prevent fluid leaks.

6.2.3.4 Accessibility

The columns are usually quite high and can therefore pose an accessibility hazard to workers and technicians. To reduce the risk of injury, safety railings should be added on the distillation column, in the case where maintenance would be required.

6.3   Pollution Prevention Techniques

Recovery devices, such as condensers, absorbers, adsorbers and incinerators, can be used to recover potential air pollutants before they are released into the environment [4]. The fuel gas emitted from the process could be recovered and used as an energy source for the fired heater, instead directly flaring all of it to the atmosphere. Leakage detection equipment could be installed throughout the system to prevent large chemical spills. Finally, there should be as much recycling of unreacted components and process integration in the system as possible, including raw materials, solvents, steam and water, to avoid the generation of large amounts of waste.

6.4   Life Cycle Analysis

6.4.1   Raw Material Acquisition

The process selected to produce toluene only requires propane as raw materials. Propane is extracted from natural gas and used as an intermediate to produce petrochemicals, which in turn have various uses. Propane is typically compressed to its liquid form in order to facilitate transportation [65]. To facilitate the process of transporting the raw material to the plant, the plant should be built in close proximity to a source of liquefied petroleum gases or it could be integrated within a natural gas facility.

6.4.2   Processing

Emissions during the processing steps are less likely to occur since most units are operated under vacuum [4]. Moreover, several recovery devices are used to recover potential air pollutants, such as toluene. These unit operations may include condensers, absorbers, adsorbers as well as incinerators [4].

6.4.3   Storage

Most toluene emissions produced from petroleum fractions are generated during the loading and storage operations as well as equipment leaks [4]. Toluene should be stored in mild steel or stainless steel containers [6] to avoid leakage of the flammable product. Moreover, it should be stored in a cool environment, well below its auto-ignition temperature of 480°C, and far away from heat and ignition sources.

6.4.4 Product Life

Approximately 86% of the toluene produced is eventually released into the atmosphere, where its lifetime varies between four days to several months, depending on the altitude and the season [4]. Approximately 65% of the toluene released in the environment is from inadvertent sources, including vehicle and aircraft exhaust, chemical spills and cigarette smoke. Industrial processes that use toluene as a raw material are responsible for 33% of the emissions, and the last 2% is emitted from toluene production facilities [4]. Toluene can contaminate soil if petroleum spills were to occur or underground storage tanks were to leak. It can also be released in water in the event of chemical spills originating from petroleum products as well as discharges of industrial effluent. In fact, it was estimated that approximately 90% of the toluene released in water in the United States resulted from gasoline and oil spills [64]. However, the majority of toluene emissions will be released into the atmosphere, as soil and water contamination mostly follow accidents.

6.4.5 Waste Management and End of Life

There should be as much recycling in the system as possible to avoid waste and for the process to be as efficient as possible. Raw materials, solvents, steam and cooling water can all be recycled within the process. If chemicals are to be disposed, one should follow the hazardous waste disposal instructions as indicated in the material safety data sheets (refer to Appendix I). In case of spills, sand and clay may be used as an absorbent.

6.5   HAZOP Analysis

A hazard and operability study (HAZOP) is a common methodology used in risk and safety analysis. It is a qualitative technique, which allows to identify possible accident scenarios and evaluate their corresponding risk. When performing a HAZOP analysis, a systematic approach is used with specific guidewords as well as possible causes and consequences, in order to investigate process deviations [66].

A HAZOP analysis was performed on the reactor and the fired heater used to preheat the reactor inlet feed and each stream between the four stages of the reactor. The endothermic reactions greatly reduce the possible hazards associated to the reactor system, since there are no risks for a runaway reaction to occur. However, it is still of great importance to examine the possible scenarios which may occur, in order to prepare solutions ahead of time. The results of the HAZOP analysis are tabulated in Table 26 for the reactor and Table 27 for the fired heater.

Table 26 – HAZOP analysis on reactor

Unit Operation Operating temperature Operating pressure	Reactor (R-101) 500-550°C 100-200 kPa
Purpose	The reactor is a radial flow moving bed reactor in which raw material (propane/butane) enters in addition to recycled material to undergo aromatization. The reactor is adiabatic and hosts an endothermic reaction. The gas-phase reaction follows Eley-Ridel kinetics as it flows through the bed of catalyst. Under normal operating conditions, the reactor output consists mainly of fuel gas (methane, ethane) and aromatics (benzene, toluene, xylenes).

Guide Word	Deviation	Cause	Consequence	Action
Flow				
No	No flow at the reactor outlet	Downstream blockage (eg. valve failure)	Pressure buildup in the reactor leading to increased stress on reactor vessels	The reactor should be equiped with a pressure relief valve that redirects the flow appropriately to a flaring system
No	No flow at the reactor inlet	1) Pipe rupture/leakage 2) Process valve upstream is fully closed	No reaction	Shut process down and fix pipe or make sure the valve is well controlled
Less of	Reduced flow rate to reactor	1) Pipe rupture/leakage 2) Process valve upstream is too closed	Lower process throughput	Shut process down and fix pipe or make sure the valve is well controlled
More of	Increased flow rate to reactor	Surge in recycle pump	1) Lower residence time in the fired heater leading to lower conversions 2) Faster catalyst deactivation	Operate the recycle pump in parallel and ensure that the other pump gets used

Guide Word	Deviation	Cause	Consequence	Action
Temperature				
Less	Decreased temperature at the reactor inlet	1) Decrease in fuel gas provided to the fired heater 2) Fire heater failure/flame goes out in the fired heater	Lower reactor conversion	Small quantities of fuel gas could be contained in storage tanks to ensure that fuel gas is always available
More	Gas is overheated in fired heater prior to entering the reactor or in the fired heaters inbetween stages	1) Increase in fuel gas provided to fired heaters due to valve failure	1) May melt the stainless steel reactor vessels and cause an explosion 2) May lead to catalyst decay 3) Increases duty of heat exchangers downstream and affect performance of other units	Ensure that the fired heater implements an adequate control strategy to prevent overheating of the reactor inlet stream
	External fire causes the reactor to be in a hot environment	1) A fired heater fails and fire propagates through dust or air to the reactor	1) May lead to failure of the reactor vessels	Reactor should be positioned in a location where fire propagation risks are limited, sources of dust should be identified and eliminated

Guide Word	Deviation	Cause	Consequence	Action
Pressure				
Less	Lower pressure than expected in the reactor	1) Faulty valve upstream 2) Pressure relief valve defect	Lower conversion	Ensure that pressure control is implemented via pressure control valves to ensure that the pressure in constant
More	Higher pressure than expected in the reactor	1) Gas is overheated in the fired heater 2) Blockage downstream (e.g. valve failure) 3) Catalyst bed blockage (packed too tightly)	Increased stress on reactor vessels may lead to vessel failure and explosion	The reactor should be equiped with a pressure relief valve that redirects the flow appropriately to a flaring system
Reaction				
No	No reaction takes place in the reactor	1) The catalyst is older than its lifetime 2) Failure of the regeneration unit 3) The wrong catalyst is shipped to the plant	Severe impact of process profitability no product is produced	Regeneration should be monitored and catalyst should be sampled at given intervals to assess its activity

Table 27 – HAZOP analysis on fired heater

Unit Operation Operating temperature Operating pressure	Fired Heater (FH-101) 400-550°C 100-200 kPa			
Purpose	Given that the propane aromatization reaction is globally endothermic, the reactants must be reheated periodically in order to provide the necessary to the reaction. The high temperatures required justify the need for a fired heater, instead of a simple heat exchanger.			
Guide Word	**Deviation**	**Cause**	**Consequence**	**Action**
Flow No	Flow is blocked at the inlet of the fired heater	1) Pipe failure upstream (leak, breakage) 2) Valve failure or valve is closed upstream	Tube failure inside the fired heater	Consider a mechanism with an alarm that detects abnormal rises in temperature; the process should stopped
No	Flow is blocked at the outlet of the fired heater	1) Valve failure downstream 2) Flow is blocked in the following reactor stage	The gas in the fired heater overheats, pressure increases and may lead to failure of tube inside fired heater and explosion	Consider a mechanism with an alarm that detects abnormal process at the outlet; the process should stopped
Less of	Flow rate through fired heater is lower than expected	1) Leak in pipe upstream 2) Recycle pump failure 3) Aperture of valve upstream is too small	The gas overheats due to higher residence time, may damage catalyst in reactor and damage reactor	Stop the process and fix broken pipe; recycle pump should have a spare; flow control valve at inlet should be properly control to provide the right flowrate

Guide Word	Deviation	Cause	Consequence	Action
Flow More of	Flow rate through fired heater is higher than expected	1) Recycle pump surge 2) Increase in propane fed to the plant	Unstable operation	Pumps should have a spare and the flowrate of propane fed to the process should be properly controlled
Temperature Less	Temperature of the stream leaving the fired heater is lower than expected	1) Fuel gas fed to the fired heater is decreased due to pipe rupture 2) Fired heater flame goes out	1) Lower conversion in the next reactor stage	Ensure the fuel flowrate to the fired heater is properly controlled; an auto-ignition mechanism should be installed so that the flame can be restarted if it goes out
More	Temperature of the stream leaving the fired heater is higher than expected	1) Fuel gas fed to the fired heater is increased	1) High temperature may lead to faster catalyst deactivation or catalyst melting 2) Higher temperature in reactor stage downstream may lead to vessel failure	The flowrate of propane fed to the process should be properly controlled
Pressure More	Pressure in the fired heater is increased	Blockage downstream	Tube may fail inside the fire heater, leading to leakage of highly flammable gas which may cause an explosion	Interlock with sudden pressure drop alarm and shut down

CHAPTER 7
CAPITAL ESTIMATE
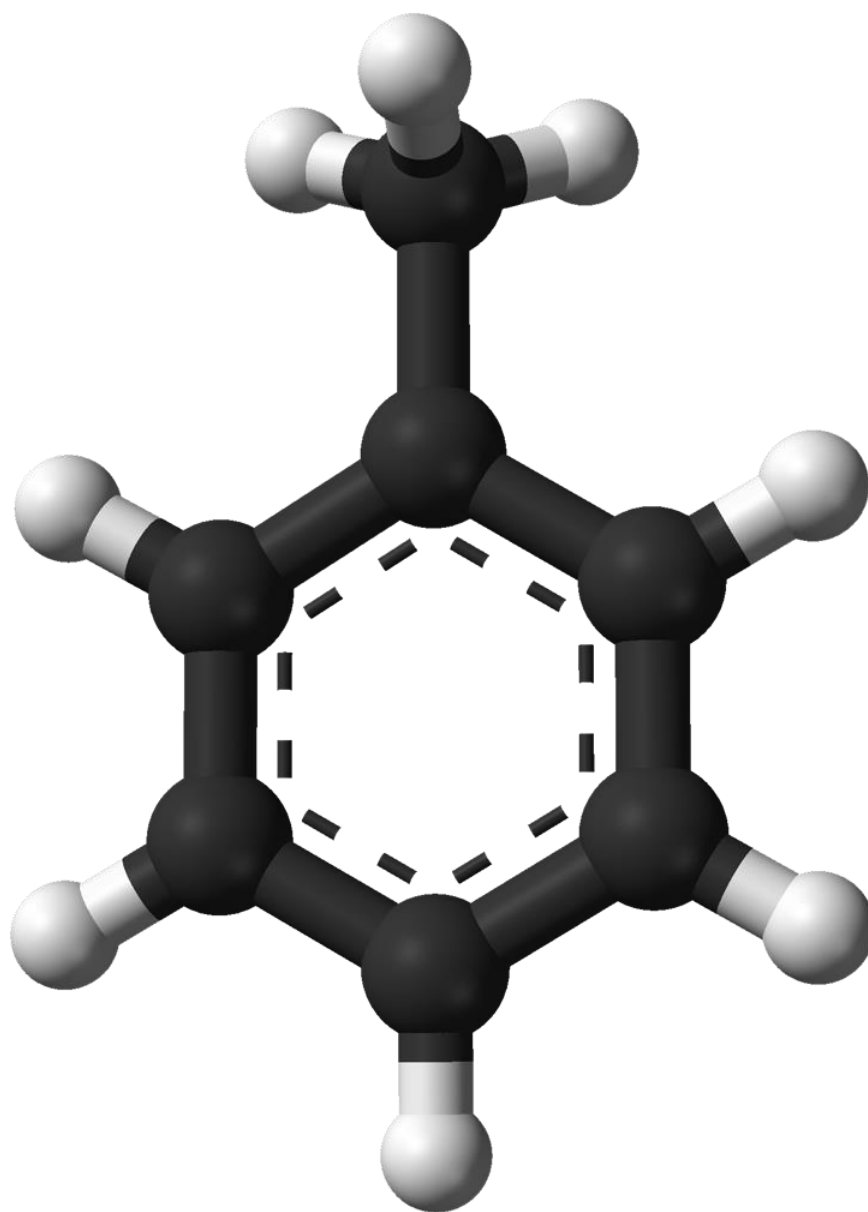
The cost of process equipment was determined using the bare module factor approach, as suggested by Guthrie [28]. This method provides a good preliminary estimate for the cost of a new chemical plant, since it relates to the specific equipment type, the system pressure and the materials of construction used.

7.1 Equipment Purchase Cost

The first step in determining the capital cost of a plant is to determine the purchase cost of each piece of equipment. The purchase cost, C_p^o, depends on constants that are specific to each equipment, as well as their capacity, as demonstrated in Equation 7-1 [28].

$$log_{10} \, C_p^o = K_1 + K_2 log_{10} \, (A) + K_3 [log_{10} \, (A) \,]^2 \tag{7-1}$$

Where K_1, K_2 and K_3 are constants, and A is the capacity of the equipment.

The following Table 28 lists the capacity term associated with each type of equipment present in the plant.

Table 28 – Capacity of major equipment

Equipment Type	Capacity Term
Heat Exchangers	Area
Pumps and Pump Motors[1]	Shaft Work
Process Vessels[2]	Volume
Distillation Column Internals	Area

[1] Including spare pumps

[2] Includes any reactor, reflux drum, reboiler vessel and distillation column.

Using Equation 7-1 with respective capacity terms determined in UniSim and constant parameters provided in Turton *et al.*, the purchase cost was estimated, which allowed to calculated the bare module cost for each piece of equipment [28].

7.2 Equipment Bare Module Cost

The bare module cost, C_{BM}, represents the total purchase cost of a piece of equipment considering the pressure and material of construction, and is determined with Equation 7-2 [28].

$$C_{BM} = C_p^o F_{BM} = C_p^o (B_1 + B_2 F_M F_P) \tag{7-2}$$

Where F_{BM} is the bare module factor, which accounts for the pressure of the system (through F_P) and the material of construction used (through F_M). B_1 and B_2 are constants specific to the type of equipment.

It is crucial to consider the design pressure of each unit since it is proportional to their price. For heat exchangers and pumps, Equation 7-3 can be used to determine the pressure factor [28].

$$log_{10} F_P = C_1 + C_2 log_{10} (P) + C_3 [log_{10} (P)]^2 \tag{7-3}$$

Where F_P is the pressure factor, C_1, C_2 and C_3 are constants, and P is the pressure of the equipment. To determine the pressure factor of process vessels, additional factors must be considered such as the corrosion allowance, the thickness and the allowable stress. This is demonstrated with Equations 7-4 and 7-5 [28].

$$F_P = \frac{\frac{(P+1)D}{2SE - 1.2(P+1)} + CA}{t_{min}} \tag{7-4}$$

$$t = \frac{PD}{2SE - 1.2P} + CA \tag{7-5}$$

Where F_P is the pressure factor, P is the pressure (barg), D is the diameter of the vessel, CA is the corrosion allowance, S is the allowable stress, E is the welding efficiency, t is the thickness and t_{min} is the minimum thickness.

The units in this plant operate at a pressure ranging from 101.2 kPa to 260 kPa. Therefore, the pressure factor is either equal to one, which means that it does not affect the cost of the unit, or it is slightly above one, indicating that it increases the bare module cost of the unit.

The material of construction also affects the bare module cost. Since the chemicals used in the process are compatible with most materials, the base case material, carbon steel, was the material of choice to reduce the equipment cost as much as possible. However, for equipment operating at

93

high temperatures (above 200°C), stainless steel was chosen to ensure the material would not melt or degenerate at high temperatures. The material factor can be determined using a graphical method with Figure 36.
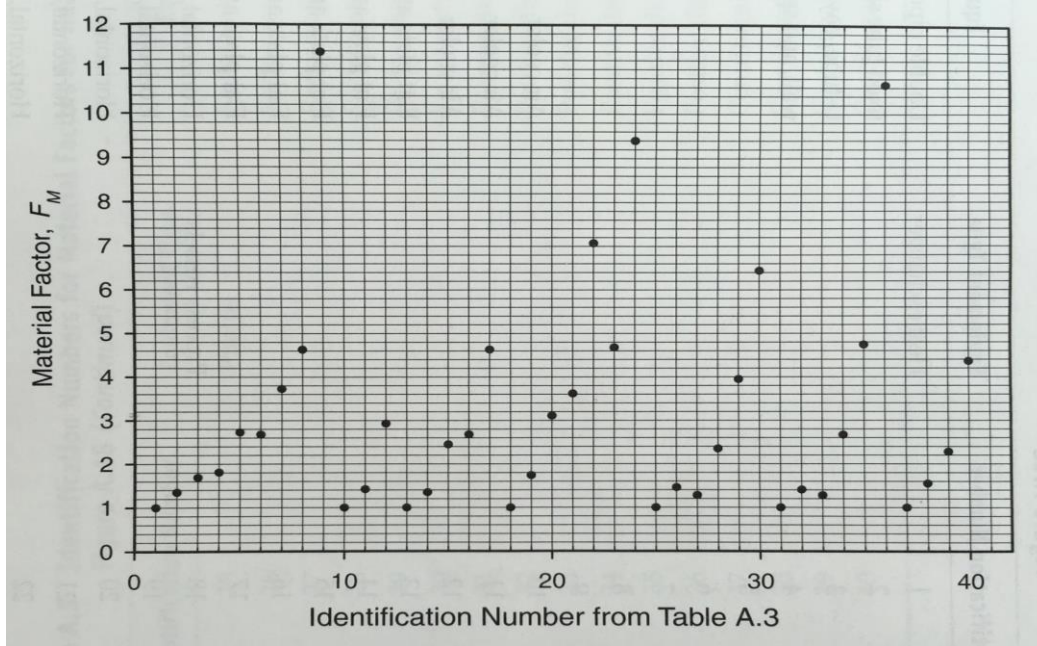
Figure 36 – Material factor of various equipment [28]

Therefore, the material of construction for the heat exchanger, the fired heater and the reactor increased the bare module cost of the equipment.

The bare module cost can also be evaluated at a base case, $C_{BM}°$, for which $F_P=1$ and $F_M=1$.

The constants provided in Turton *et al*. are for the year 2001. Therefore, in order to determine the corresponding cost for 2016, the bare module cost was adjusted using the Chemical Engineering Plant Cost Index (CEPCI), as shown in Equation 7-6 [28].

$$C_{BM\,2016} = C_{BM\,2001}\left(\frac{CEPCI_{2016}}{CEPCI_{2001}}\right) = C_{BM\,2001}\left(\frac{537.1}{397}\right) \qquad (7\text{-}6)$$

Using Equation 7-2 with constant parameters provided in Turton *et al.*, the bare module cost was estimated at the base conditions and at the process conditions [28]. It was then corrected using Equation 7-6, in order to determine the current cost. These costs are listed in Table 29 to Table 32, for the pieces of equipment present in Section 100 to 400 of the plant, respectively.

Table 29 – Bare module cost of 2016 for equipment in Section 100

Equipment	C_{BM}^o	C_{BM}
HX-101	$75,876	$331,171
FH-101	$1,968,955	$1,968,955
P-101	$21,480	$26,403
R-101 (Stage 1)	$357,282	$1,013,251
R-101 (Stage 2)	$524,207	$1,492,964
R-101 (Stage 3)	$674,029	$1,782,968
R-101 (Stage 4)	$1,303,843	$3,524,495

Table 30 – Bare module cost of 2016 for equipment in Section 200

Equipment	C_{BM}^o	C_{BM}
V-201	$11,701	$11,701

Table 31 – Bare module cost of 2016 for equipment in Section 300

Equipment		C_{BM}^o	C_{BM}
T-301	Vessel	$26,780	$26,780
	Trays	$36,667	$36,667
	Condenser	$88,483	$88,483
	Reflux Drum	$10,072	$10,072
	Reflux Pump (and spare)	$21,480	$26,403
	Reboiler	$95,689	$95,689
	Reboiler Vessel	$6,635	$6,635

T-302	Vessel	$11,031	$11,031
	Trays	$48,777	$48,777
	Condenser	$88,483	$88,483
	Reflux Drum	$7,572	$7,572
	Reflux Pump (and spare)	$21,480	$26,403
	Reboiler	$95,689	$95,689
	Reboiler Vessel	$9,066	$9,066

Table 32 – Bare module cost of 2016 for equipment in Section 400

Equipment		C_{BM}^o	C_{BM}
T-401	Vessel	$18,552	$18,552
	Trays	$42,682	$42,682
	Condenser	$88,483	$88,483
	Reflux Drum	$9,165	$9,165
	Reflux Pump (and spare)	$21,480	$26,403
	Reboiler	$109,519	$109,519
	Reboiler Vessel	$14,866	$14,866

T-402	Vessel	$28,607	$28,607
	Trays	$39,873	$39,873
	Condenser	$83,133	$83,133
	Reflux Drum	$14,358	$14,358
	Reflux Pump (and spare)	$21,480	$26,403
	Reboiler	$100,665	$100,665
	Reboiler Vessel	$15,602	$15,602

As demonstrated in Table 29 through Table 32, the cost of units varies a lot, mostly due to the size and operating conditions of the equipment. The most expensive piece of equipment in the plant is the reactor, R-101, which has a total bare module cost of $7.81 million for all four stages. It represents such a high cost because it is a very complex piece of equipment, since each of the four stages is composed of three vessels, for a total of 12 process vessels. Moreover, it operates at high pressures and temperatures, meaning that the vessels must be thicker and also a more robust material must be selected to withstand the high temperatures of the chemicals.

The fired heater, FH-101, also represents a significant cost of $1.97 million because it has a large capacity and must be made of stainless steel. It was determined that a single larger fired heater would be designed with heat integration instead of many smaller ones to reduce the capital cost as much as possible.

Finally, the distillation columns are also quite expensive because they require many additional pieces of equipment, such as the condenser, reflux drum and pump, reboiler and reboiler vessel. However, they were designed to operate at moderate pressures and relatively low temperatures. Therefore, the vessels do not need to be made very thick and carbon steel can be selected as a good option for the material of construction. The bare module cost for all four distillation columns is estimated at $1.20 million, each column ranging from $290 to $310 thousand.

7.3 Total Capital Costs

The total module cost, C_{TM}, represents the fixed capital investment, and can be calculated using Equation 7-7 [28].

$$C_{TM} = 1.18 \sum_{i=1}^{n} C_{BM,i} \qquad (7\text{-}7)$$

The factor 1.18 accounts for the contingency costs and fees. The plant's total module cost was estimated at $13,390,565.

The grassroot cost, C_{GR}, which is the cost associated to building a new plant can be evaluated from Equation 7-8 [28].

$$C_{GR} = C_{TM} + 0.50 \sum_{i=1}^{n} C_{BM,i}^{o} \qquad (7\text{-}8)$$

The factor 0.50 represents auxiliary facilities costs, which include site development, auxiliary buildings, off-sites as well as utilities. The plant's grassroot cost was estimated at $16,497,420. The grassroot cost can be used as an estimate of the fixed capital investment required for the plant, which is used to perform a thorough economic and profitability analysis.

The following Figure 37 represents the breakdown of the grass root cost for each section of the plant.
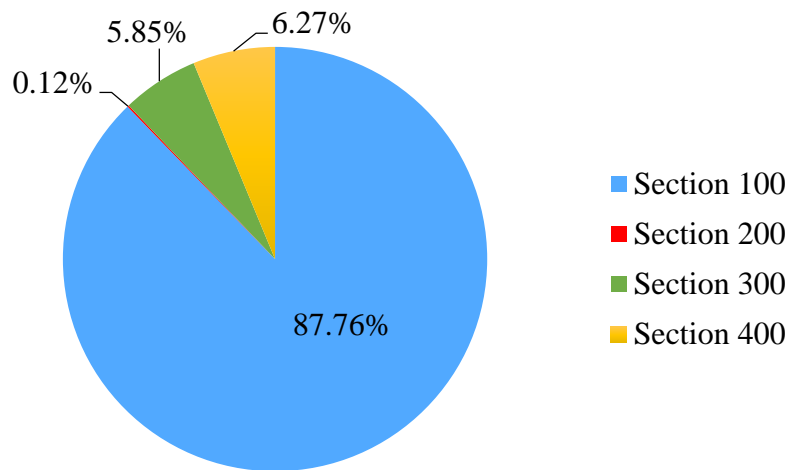

Figure 37 – Breakdown of grass root cost per section of the plant

As can be concluded from Figure 37, most of the cost originates from Section 100 of the plant, more specifically from the reactor. Since the reactor has such a complex design and requires multiple stages, it is to be expected that it corresponds to most of the capital costs.

7.4 Scale Up

Due to the flow rate design limitations of the reactor, the plant simulation could not be performed for the desired high capacity production rate, as explained in Chapter 3 and Appendix C. Therefore, the costs previously presented in this chapter correspond to a BTX production rate of 18,343 metric tons per year. Since the process could not be simulated in UniSim for a desired BTX production rate of 100,000 metric tons per year, the individual capacities for each unit are not representative of what they should be and cannot be individually determined for each unit. However, the total module cost and grass root cost can be scaled-up using the six tenth rule, as demonstrated in Equation 7-9 [28].

$$Cost_{Scaled-Up} = Cost_{Current} \left(\frac{Production\ Rate_{Scaled-Up}}{Production\ Rate_{Current}} \right)^{0.6} \qquad (7\text{-}9)$$

With this correction factor, the total module cost and the grass root cost were estimated at $37,043,158 and $45,637,847, respectively.

CHAPTER 8
OPERATING COSTS
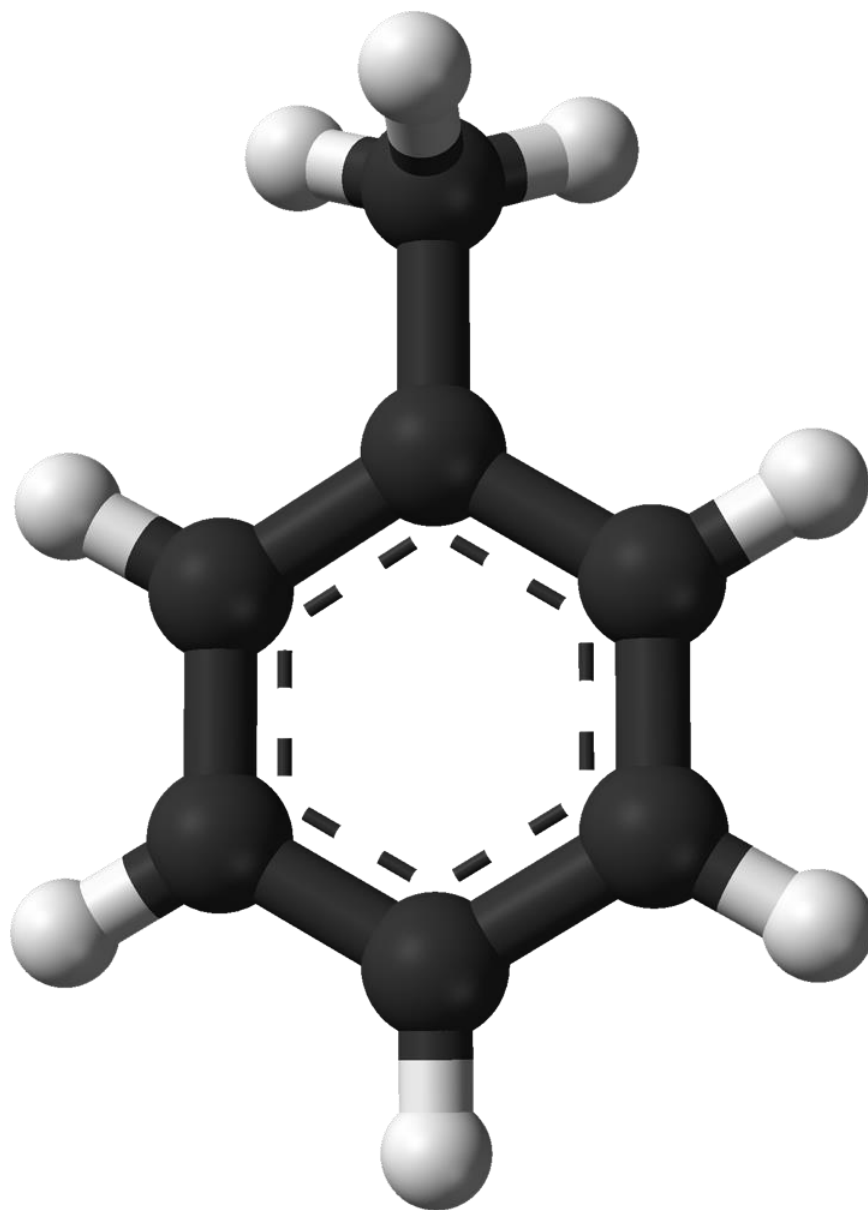
In order to perform a full economic feasibility analysis, the everyday costs must be considered in addition to the capital cost of the plant.

8.1 Operating Labour Costs

The operating labour costs, C_{OL}, depend on the number of operators required, which is related to the number of equipment in the plant through Equation 8-1 [28].

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{NP})^{0.5} \qquad (8\text{-}1)$$

Where N_{OL} is the number of operators per shift, P is the number of processing steps involving solids and N_{NP} is the number of processing steps not involving solids. The pieces of equipment that need to be considered when calculating N_{NP} are compressors, towers, reactors, heaters that aren't using steam and heat exchangers. With the number of operators needed and their respective salary, the operating labour cost was estimated with Equation 8-2 [28].

$$C_{OL} = N_{OL} \times total\ number\ of\ operators\ needed \qquad (8\text{-}2)$$
$$\times\ operator\ salary$$

Where the total number of operators needed was calculated based on the number of operators per shift and the number of shifts per year. It was estimated that a total of 14 operators would be needed to cover the various shifts required to achieve a plant operation time of 24 hours a day for 50 weeks per year. With an hourly wage of operators given as \$30/h, the total operating labour was estimated at \$873,600 per year.

8.2 Utility Costs

The utility costs, C_{UT}, can easily be determined by multiplying the amount required by the cost of each individual utility, as shown in Equation 8-3 [28].

$$C_{UT} = amount\ required \times cost \times SF \qquad (8\text{-}3)$$

Where SF is the stream factor, which considers the two weeks of downtime during the year.

Table 33 summarizes the amount of utilities required for a production rate of 18,343 metric tons per year, and their respective cost.

Table 33 – Utilities and their associated cost (production rate of 18,343 metric tons per year)

Type of Utility	Amount Required	Cost ($/year)
Cooling Water	12,580 kg/h	$2,100
Liquid Nitrogen	6,604 kg/h	$8,978,036
Low Pressure Steam	190 kg/h	$63,438
High Pressure Steam	1,912 kg/h	$653,240
Electricity	0.6502 kW	$445

In order to reduce the utility costs as much as possible, heat integration was performed. This allowed to exchange heat between the process streams as much as possible, before utilizing utilities. Moreover, the fuel gas required for the fired heater is a by-product of the process, therefore eliminating the need to purchase some. Liquid nitrogen is required for three of the four distillation columns because it is the only refrigerant available at temperatures low enough to condense the distillate. The amount of electricity required for the pumps is very small. This can be due to the fact that the estimated velocity in the pipes when designing the pumps is very small because the flow rates are fairly small as well, or due to assumptions made while sizing the pumps with Bernoulli's principle. The total utility costs were estimated at $9,538,563 per year, with reasonable heat integration.

With the scale up of the production rate, as explained in Chapter 7, it was estimated that the cost of utilities would increase linearly. Therefore, the cost of utilities for the corrected BTX production rate can be estimated to be $52,864,502 per year.

8.3 Waste Treatment Costs

Any process stream that was not recycled or sold as a valuable product has to be disposed of. This includes the purge stream for the recycle of propane, along with any excess fuel gas which is not used in the fired heater. The waste treatment cost was estimated by multiplying the mass

flow rate of the waste stream and the price of each disposal or treatment technique, as shown in Equation 8-4 [28].

$$C_{WT} = amount\ required \times cost \times SF \tag{8-4}$$

Table 34 summarizes the amount of waste produced and its respective disposal cost.

Table 34 – Waste treatment and its associated costs (production rate of 18,343 metric tons per year)

Type of Waste	Amount Produced (kg/h)	Cost ($/year)
Hazardous Waste Disposal	2,222	$5,065,878

Therefore, the total waste treatment cost was estimated at $5,065,878 per year. Again, this was corrected for the desired production rate of BTX assuming a linear relationship. The scaled-up waste treatment cost is estimated at $27,616,582 per year.

8.4 Raw Materials Costs

The cost of raw materials can be determined in a similar fashion as the cost of utilities and waste treatment, as shown in Equation 8-5 [28].

$$C_{RM} = amount\ required \times cost \times SF \tag{8-5}$$

Table 35 summarizes the cost of raw materials in this process.

Table 35 – Raw materials and their associated cost (production rate of 18,343 metric tons per year)

Raw Material	Amount Required	Cost ($/year)
Propane	4,410 kg/h	$12,821,442
HZSM-5	177,700 kg/2 years	$7,152,425

In order to reduce the cost of raw materials, a recycle stream was added in the process. With the addition of the recycle stream, a smaller amount of fresh propane was required, and the overall conversion of the process was increased, therefore generating more revenues from the resale of BTX. Since the catalyst must be replaced every two years, its cost was divided equally over a period of one year. The cost of raw materials was estimated at $19,973,867 per year for this

process. Assuming a linear correlation, the cost of raw materials was corrected at $108,887,328 per year, for the desired BTX production rate.

8.5 Manufacturing Costs

The total manufacturing costs include direct and fixed manufacturing costs as well as general expenses. Direct manufacturing costs depend on the production rate. Such costs include operating labour, raw materials, utilities, and more. Fixed manufacturing costs represent factors that are independent of the production rate, such as depreciation, taxes and insurance as well as overhead costs. Finally, general expenses are related to managerial and administrative activities and are therefore not directly related to the production rate of the process [28]. The total manufacturing costs, with and without depreciation, can be estimated with Equation 8-6 and 8-7 [28].

$$COM = 0.280FCI + 2.73C_{OL} + 1.23(C_{UT} + C_{WT} + C_{RM}) \qquad (8\text{-}6)$$

$$COM_d = 0.180FCI + 2.73C_{OL} + 1.23(C_{UT} + C_{WT} + C_{RM}) \qquad (8\text{-}7)$$

Where COM is the cost of manufacture, COM_d is the cost of manufacture without depreciation, FCI is the fixed capital investment, C_{OL} is the operating labour costs, C_{UT} is the cost of utilities, C_{WT} is the waste treatment cost and C_{RM} is the cost of raw materials.

The total manufacturing costs, with and without depreciation, were estimated at $248,086,672 and $243,522,887 per year, respectively, for a scaled-up production rate of 100,000 metric tons per year.

The direct, fixed and general manufacturing costs can be estimated using Equations 8-8 through 8-10, respectively [28].

$$Direct = C_{RM} + C_{WT} + C_{UT} + 1.33C_{OL} + 0.03COM + 0.069FCI \qquad (8\text{-}8)$$

$$Fixed = 0.708C_{OL} + 0.068FCI + depreciation \qquad (8\text{-}9)$$

$$General = 0.177C_{OL} + 0.009FCI + 0.16COM \qquad (8\text{-}10)$$

For a scaled-up BTX production rate of 100,000 metric tons per year, the yearly direct, fixed and general manufacturing costs were estimated to be $201,121,912, $8,285,667 and $40,259,235,

respectively. Figure 1 illustrates the percentages of these expenses with respect to the total manufacturing costs.
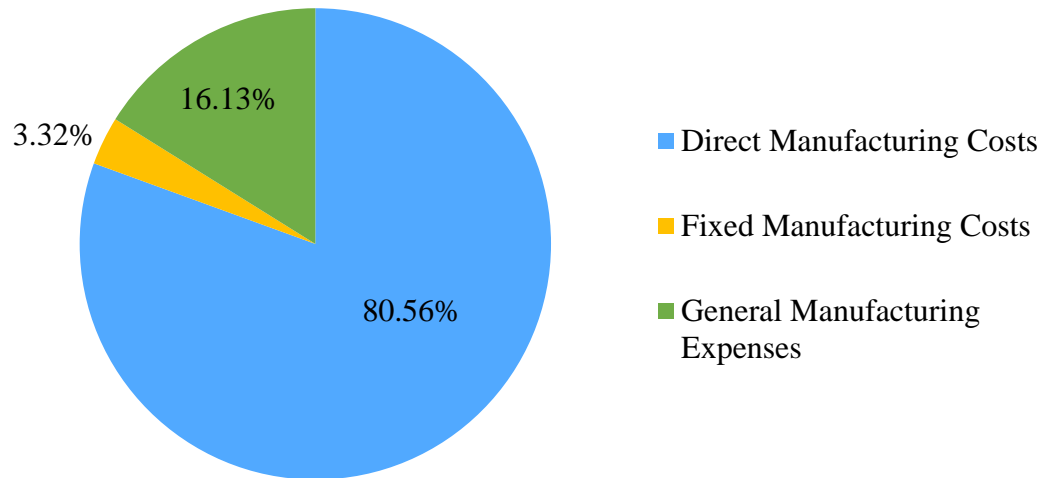
Figure 38 – Breakdown of the total manufacturing costs

The majority of the manufacturing costs are associated with the direct manufacturing costs, which is to be expected since the cost of raw materials, utilities, waste treatment and operating labour are considered in addition to the total cost of manufacturing and the fixed capital investment. The following Figure 39 demonstrates the distribution of these additional costs that were considered in the calculation of the direct manufacturing costs.

Figure 39 – Distribution of the direct manufacturing costs

8.6 Revenues

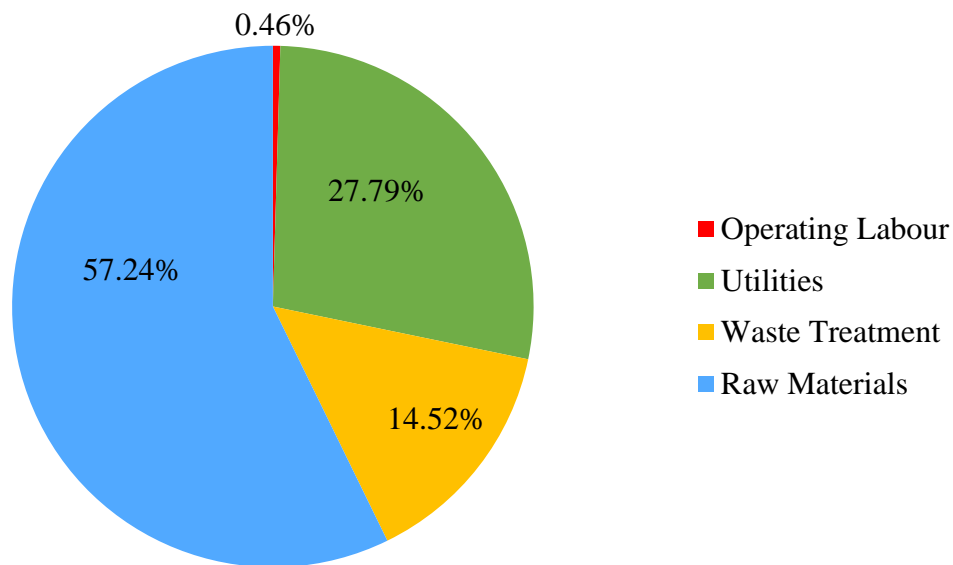The revenues generated by the resale of BTX products can be estimated with Equation 8-11 [28].

$$Revenues = amount\ produced \times cost \times SF \qquad (8\text{-}11)$$

Table 25 summarizes the revenues produced in this process.

Table 36 – BTX products and their associated resale revenue (production rate of 18,343 metric tons per year)

Product	Amount Produced (kg/h)	Revenue ($/year)
Benzene	537	$3,348,145
Toluene	1,093	$6,162,053
Xylene	547	$3,804,339

With the resale of the BTX products, a yearly revenue of $13,314,538 was estimated. Since a majority of the BTX products is more commonly used as a fuel additive for petroleum products, it only requires a minimum purity of 95%.

The total revenues were corrected for the target BTX total production rate of 100,000 metric tons per year, assuming a linear relationship. Therefore, the total revenues are estimated to be $72,584,065 per year.

CHAPTER 9
ECONOMIC EVALUATION
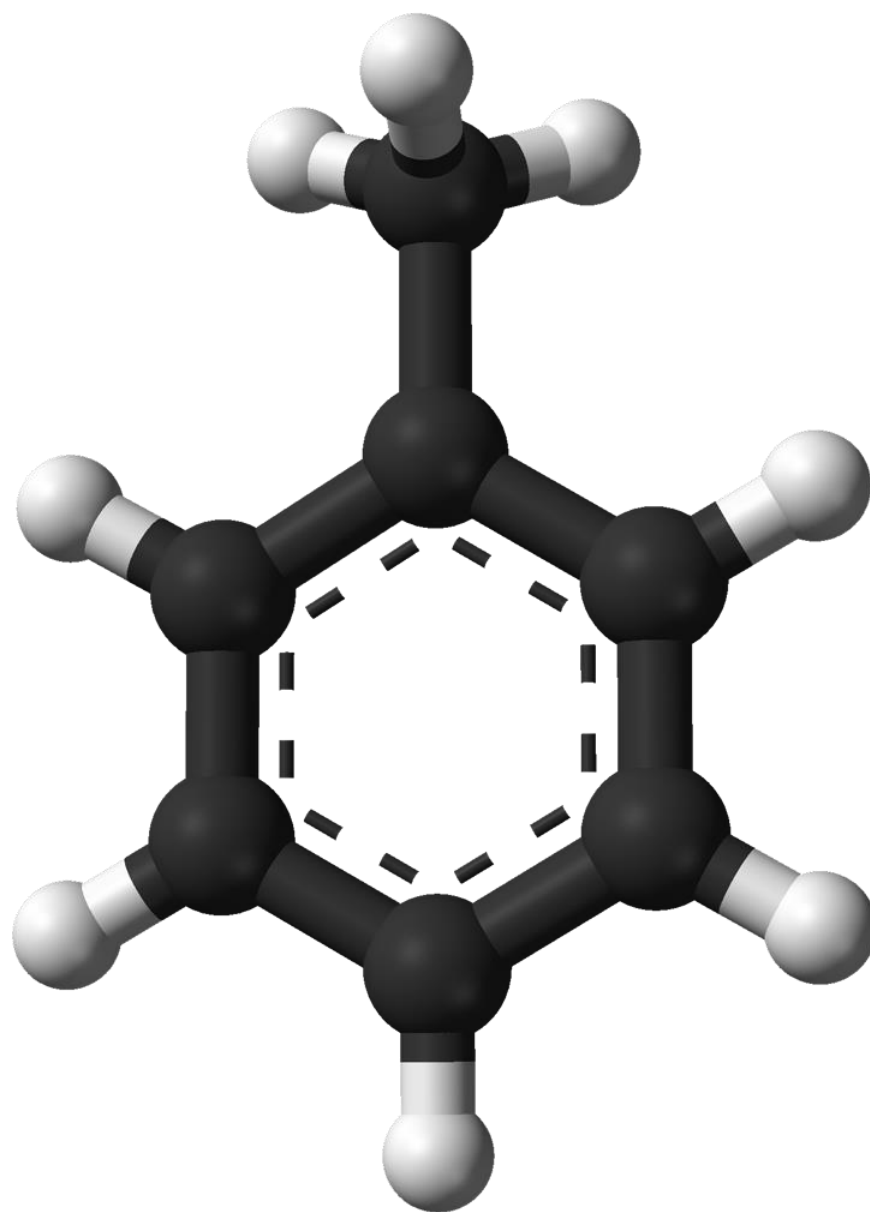
Determining whether or not the process is economically profitable is a pivotal step that must be taken prior to plant commissioning. Clearly, the venture should bring sufficient profits in a timely manner to justify the costs associated with the plant and its operations. Different process economics criteria have been developed in order to determine whether pursuing a venture is justified or not. Ultimately, the goal of any given for-profit venture is to generate profit so that there is a high incoming flow of cash [28].

A lot of care must be taken in order to account for all factors that may affect this cash flow, such as capital costs, costs of manufacturing, revenue, tax, depreciation, as well as the time value of money caused by interest and inflation [28].

This chapter is concerned with the assessment of the overall profitability of the venture for the base case and with optimization of parameters impacting it.

9.1 Assessment of the Nondiscounted Profitability

The nondiscounted method used to calculate profitability does not take the time value of money into account, making it a simple, but approximative method that applies to short, small-scale projects [28]. This method involves three criteria based on time, cash flows and interest, namely the payback period (PBP), cumulative cash position (CCP), cumulative cash ratio (CCR) and the rate of return on the investment (ROROI).

Table 37 – Nondiscounted profitability assessment criteria [28]

Criterion	Definition
Payback period (PBP)	Time required after startup to recuperate the fixed capital investment
Cumulative cash position (CCP)	Worth of the project at the end of its economic life
Cumulative cash ratio (CCR)	Cumulative cash position normalized with the fixed capital investment
Rate of return on the investment (ROROI)	Rate at which money is made from a fixed capital investment

To calculate these criteria, it is essential to have a good understanding of how the cash flows over the economic lifetime of the venture. Initial years are associated with major capital investments including the purchase of the land, fixed capital investments for the installations and equipment, as well as the working capital to allow the initiation of operations. Once operations start, investments play a lesser role and cash flows depend mostly on revenue, cost of manufacturing, tax and depreciation.

The economic analysis necessitates knowledge of various parameters. The parameters relevant to the economic analysis are tabulated in Table 38

Table 38 – Parameters related to the economic analysis

Time considerations	
Economic life (years)	12
Construction period (years)	2
Project life (years)	10
Depreciation period (years)	7
Rates	
Tax rate (%)	30
Effective interest rate (%)	6
Internal discount rate (%)	6

Cash flow diagrams (CFD) are often used to illustrate the flow of cash in a venture. It is reasonable to assume that cash flows occur in discrete amounts at the end of each year, simplifying calculations slightly.

9.1.1 Construction Phase

The beginning of the economic analysis is initiated with the purchase of the land on which the plant is to be built. This investment is made at the end of the 0th year, marking the start of the economic life of the venture. The cost of the land, assuming it is purchased in the United States for reasons outlined in Chapter 1, is estimated to $565,405, based on an area of 5.33 acres, which was determined from Shell, Imperial Oil and Suncor plants area.

The fixed capital investment without the land (FCI$_L$) is invested over the two construction years, with a 60%-40% split in the first and second year, respectively. A working capital (WC) is invested at the end of the second year in order to finance operations before any revenue is made [28]. The FCI$_L$ can be estimated to be roughly equal to the grassroots costs, given that the land purchased is bare and needs to be prepared [28]. In general, it is suggested to allow the WC to be 15-20% of the FCI$_L$ [28]. To limit risks, a conservative WC corresponding to 20% of the FCI$_L$ can be selected.

The cumulative cash flow at the end of the construction phase corresponds to the sum of the cash flows resulting from the purchase of the land, the FCI$_L$, as well as the WC. The cash position of the venture post-construction, immediately before the process starts operating, is estimated at $50.8M for the base case venture.

9.1.2 Production phase

In order to determine the profitability criteria, the cash flows of each production year must be known.

At the start of the operations, the book value of the assets is equal to the FCI$_L$. The assets are subject to depreciation over time due to the decrease in their value due to deterioration and obsolescence [67] and companies are entitled to an allowance to compensate for this loss of value. The double declining balance depreciation (DDB) method is used to distribute the depreciation over the depreciation period. The depreciation is given by the equation below [28]:

$$d_k{}^{DDB} = \frac{2}{n}\left(FCI_L - \sum_{j=0}^{j=k-1} d_j{}^{DDB}\right) \tag{9-1}$$

Where $d_k{}^{DDB}$ is the depreciation rate at year k, and n is the depreciation period, $d_j{}^{DDB}$ is the depreciation at year j. It is important to note that the depreciation rate over the last year of the depreciation period must be determined such that the book value of the assets is equal to a pre-determined salvage value.

The after-tax cash flow must be calculated to account for the costs of manufacturing, the revenue and the depreciation according to the following equation:

$$CF_{after-tax} = (R - COM_d - d)(1 - t) + d \qquad (9\text{-}2)$$

Where $CF_{after-tax}$ is the cash flow after tax, R is the revenue, COM_d is the cost of manufacturing minus the depreciation, d is the depreciation and t is the taxation rate.

The non-discounted cash flow, CF, for any production year is given by the cash flow after tax plus the investment done that year:

$$CF = CF_{after-tax} + investment \qquad (9\text{-}3)$$

It is reasonable to assume that the some money can be recovered at the end of the project. This money corresponds to a fraction of the FCI$_L$ (salvage value), the cost of the land, which does not depreciate appreciably, and the WC.

9.1.3 Nondiscounted Profitability Criteria

The discrete nondiscounted cash flows over the entire lifetime of the project at the base case are presented in Figure 40 – Yearly discrete cash flows over the economic lifetime of the venture.
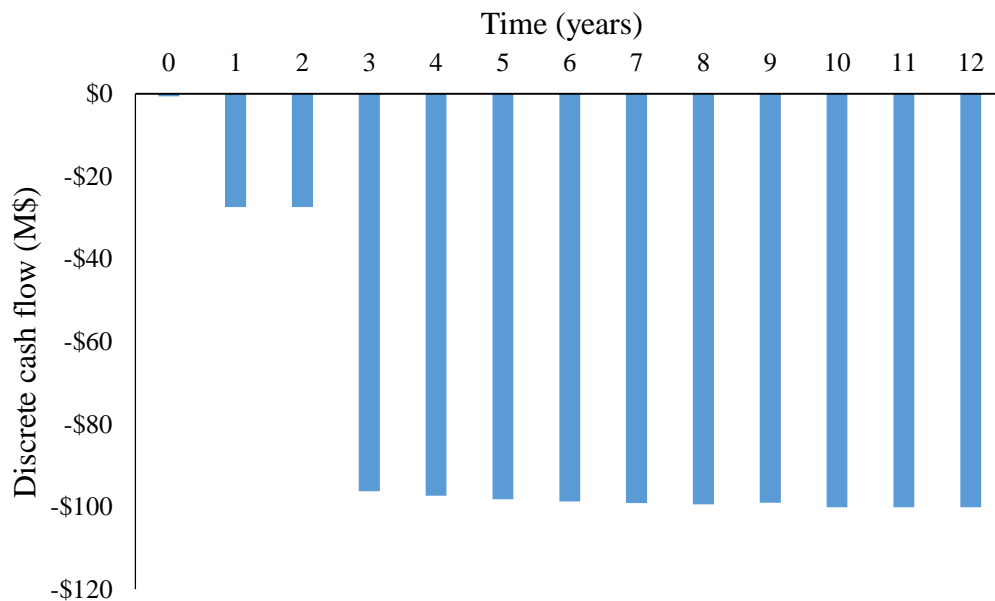

Figure 40 – Yearly discrete cash flows over the economic lifetime of the venture

The evolution through time of the cumulative nondiscounted cash flow for the venture is illustrated in Figure 41.
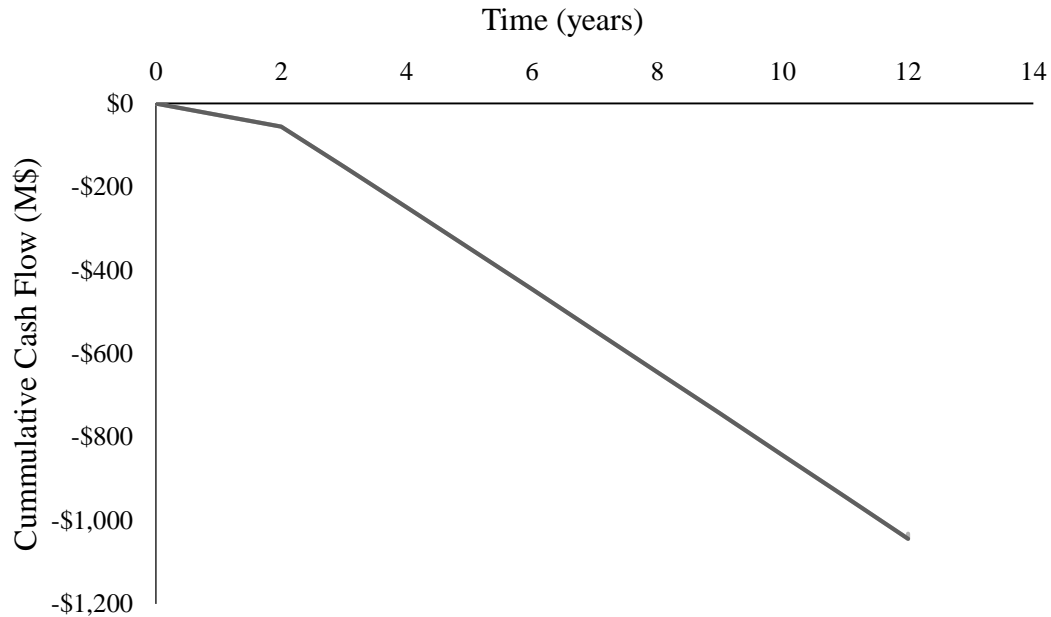

Figure 41 – Cumulative cash flow for the venture

Both Figure 40 and Figure 41 demonstrate that the yearly cash flows and the nondiscounted cumulative cash flow remains negative throughout the lifetime of the venture, suggesting from the get-go that profits cannot be achieved over the 10 years of operation.

The nondiscounted profitability criteria introduced previously are usually used to formally assess the profitability. The PBP can be determined from Figure 41, more specifically by finding the time at which the FCI_L has been recovered. In other words, the PBP occurs when the cumulative cash flow is equal to the WC and the cost of land. The PBP may be inexistent in cases where the venture is not profitable because the process operates at a loss for example.

The CCP, or the project worth at the end of the project lifetime, is often considered to be a poorer criteria than the CCR because it does not take into account the size of the fixed capital investment (FCI_L) [28]. The CCP is simply the project worth at the end of its life. The CCR is defined as follow:

$$CCR = 1 + \frac{CCP}{Cost\ of\ land\ + WC + FCI_L} \qquad (9\text{-}4)$$

The ROROI, which represents the rate at which profit is generated from the FCI$_L$, is defined as follows:

$$ROROI = \frac{Slope\ of\ average\ cash\ flow}{FCI_L} - \frac{1}{n} \qquad (9\text{-}5)$$

Where n is the project lifetime, or in this case, 10 years.

The profitability criteria are summarized in Table 39.

Table 39 – Nondiscounted profitability criteria summary

Criterion	Value
PBP (years)	Undefined[1]
CCP ($B)	-1.04
CCR	-17.9
ROROI	-2.27

[1]The payback period is never reached in the process.

All nondiscounted profitability criteria are strongly unfavourable. Since there no net profit is made during the venture, the FCI$_L$ is never recovered. For this reason, the PBP is inexistent. Furthermore, the negative CCP indicates that at the end of the venture, $685M is owed in debt. The negative CCR is consistent with the negative CCP, because it is merely the CCP normalized with the FCI$_L$. Projects with a CCR superior to 1 are potentially profitable [28], which is far from being the case for the venture of interest. Finally, the negative ROROI indicates that each dollar invested in the FCI$_L$ yields a negative amount of money, or in other words, a loss of money.

9.2 Assessment of the Discounted Profitability

In the discounted profitability analysis, the cash flows are discounted to their value at the start of the venture. This analysis is similar in many respects to the nondiscounted analysis, but yields better estimates, because the time value of money influenced by interest rates and inflation is considered. The criteria used in the discounted analysis are listed in Table 40.

Criterion	Definition
Discounted payback period (DPBP)	Time required after startup to recuperate the fixed capital investment for discounted cash flows
Discounted cumulative cash position (DCCP/NPV)	Worth of the project at the end of its economic life for discounted cash flows
Present value ratio (PVR)	Cumulative discounted cash position normalized with the fixed capital investment
Discounted cash flow rate of return (DCFROR)	Highest after-tax interest for which the cumulative discounted cash flow at the end of the project is 0

To convert the cash flow to a discounted cash flow, a relation comprising the interest rate is used:

$$P = \frac{F}{(1 + i)^n} \qquad (9\text{-}6)$$

Where P is the discounted cash flow, F is the nondiscounted cash flow, i is the yearly effective interest rate and n is the number of years elapsed since the start of the venture.
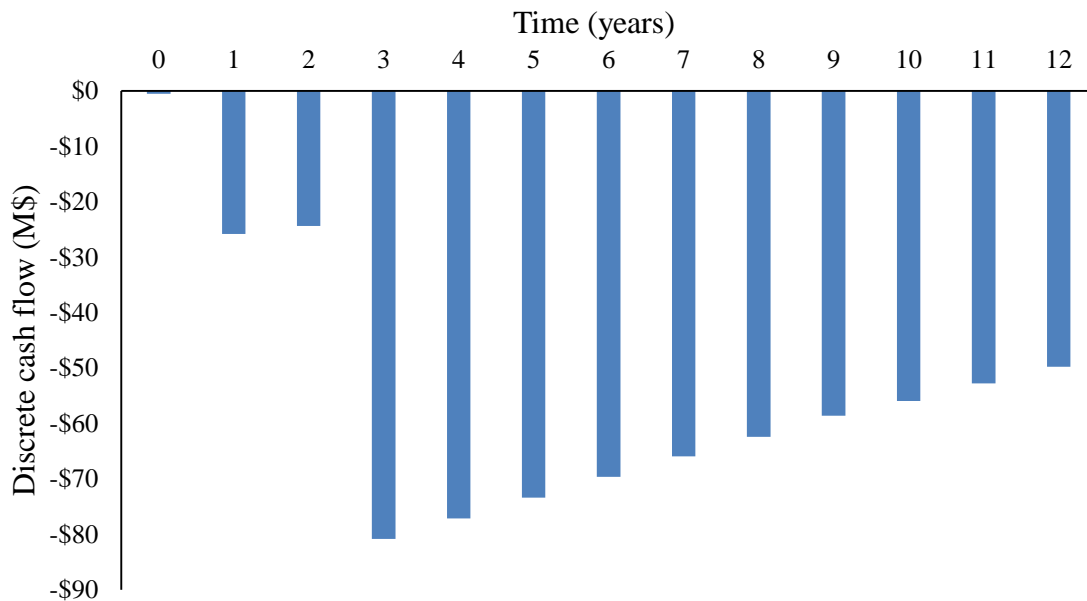

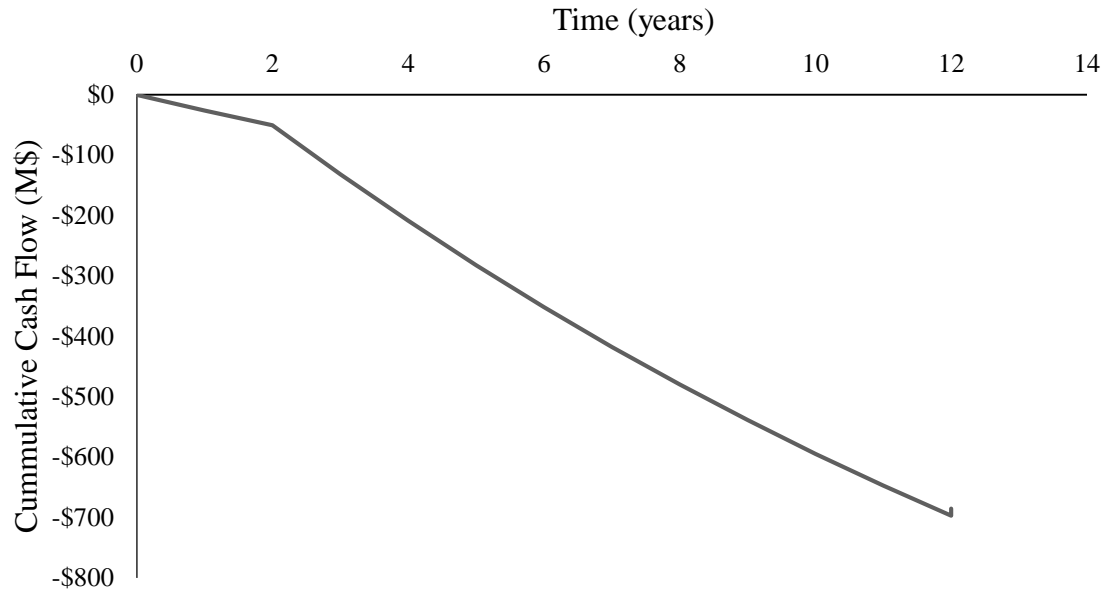Figure 42 – Discrete discounted cash flows for the venture

Figure 43 – Cumulative discounted cash flow for the venture

The DPBP is determined the same way as the PBP was in the nondiscounted analysis. In other words, it correspond to the time where the cumulative discounted cash flow is equal to the WC and the cost of the land.

The DCCP is also trivially determined, as it is the worth of the venture at the end of its lifetime.

The PVR is, much like the CCR, is the ratio of discounted positive cash flows and discounted negative cash flows. Mathematically,

$$PVR = \frac{Present\ value\ of\ positive\ cash\ flows}{Present\ value\ of\ negative\ cash\ flows} \tag{9-7}$$

The calculation of the DCFROR, however, is a little more involved. The DCFROR, or the interest rate at which the DCCP is 0, can be determined easily using Microsoft Excel's Solver.

The discounted profitability criteria are summarized in Table 41

114

Table 41 – Summary of the discounted profitability criteria

Criterion	Value
DPBP (years)	Undefined[1]
DCCP/NPV ($M)	-697
PVR	0
DCFROR	Undefined[2]

[1]The payback period is never reached in the process.

[2]No interest rate can allow to break even.

Again, the profitability criteria for the discounted analysis strongly suggest that the venture would be unprofitable. Since the cost of manufacturing outweigh the revenues throughout the venture, no net profits can be made, regardless of the time value of money. The worth of the venture at the end of its lifetime is -$697M, indicating debt. Finally, the PVR is equal to 0, because there are no positive discounted cash flows throughout the lifetime of the project. The DCFROR could not be determined, as no interest rate allows the system to reach a DCCP of zero due to the consistently negative non discounted cash flow.

9.3 Sensitivity Analysis

9.3.1. Recycle Rate

The variability of the recycle stream flow rate was quantified by observing its effect on the discounted payback period (DPBP), the cumulative discounted cash position at the end of the project (NPV) and the discounted cash flow rate of return (DCFROR). The recycle rate was varied from 5 to 68 kg/h. The recycle rate was chosen in this range to avoid total recycle of the remaining propane as accumulation would occur in the system in that instance. The effect of the variation of the recycle stream flow rate on the DPBP are not promising; the DPBP is undefined for the plant, regardless of the recycle ratio, as the fixed capital investment will never be recovered.

The effect of the recycle rate on the NPV is shown in Figure 44. The NPV is decreasing linearly with the flow rate. It should be noted that Figure 44 presents value that are very different from the base case scenario, and that they are most probably not correct. The calculations could not be

corrected because of time and staff limitations. Nevertheless, the project is definitively not profitable, regardless of the recycle mass flow.
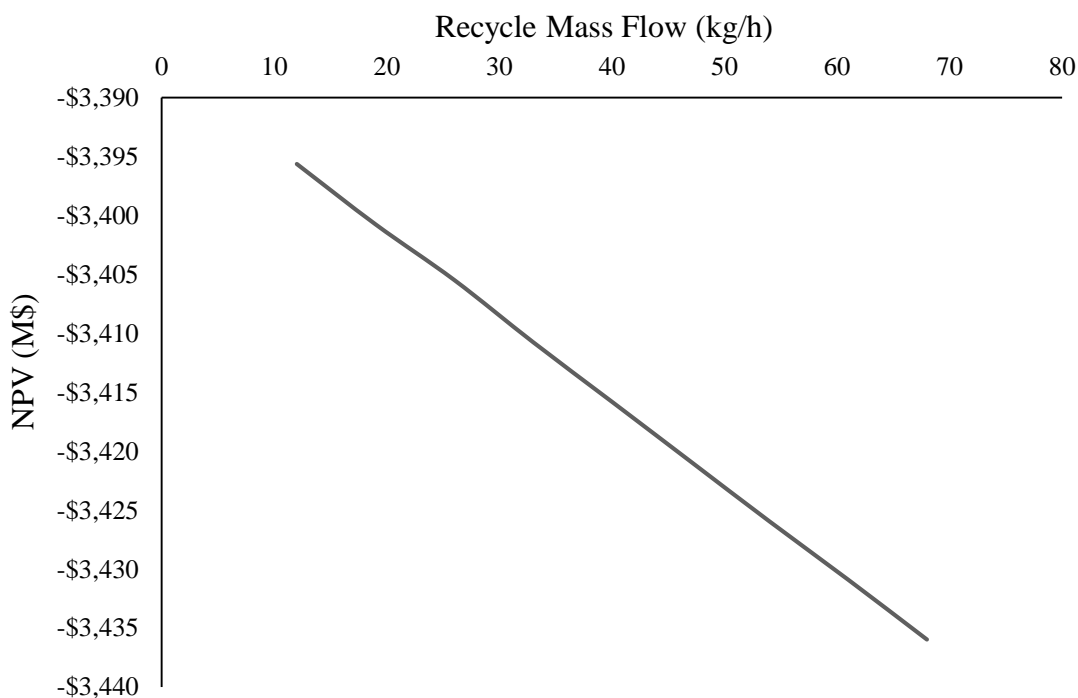

Figure 44 – Effect of recycle stream flow rate on NPV

The DCFROR is undefined as it was observed that the project NPV would never reach 0.

9.3.2 Production Capacity

The variability of the plant production capacity was quantified by observing its effect on the DPBP, NPV and DCFROR. The capacity was varied between 20% and 200% of the initial production rate of BTX, which was of 100 000 MT/yr. Similar results were obtained from the production capacity sensibility analysis and from the recycle stream flow rate analysis as, in both cases, the plant generates no profit. The discounted payback period is never going to be reached, as the cash flows of the plant are negative regardless of the production rate. Once the fixed capital investment is made, it will never be recovered. Furthermore, the DCFROR does not exist, as the net present value of the project can never reach zero. The effect of capacity on the NPV is

shown in Figure 45. The NPV decreases linearly with the plant capacity; the more the plant produces, the less its net present value at the end of the project will be.
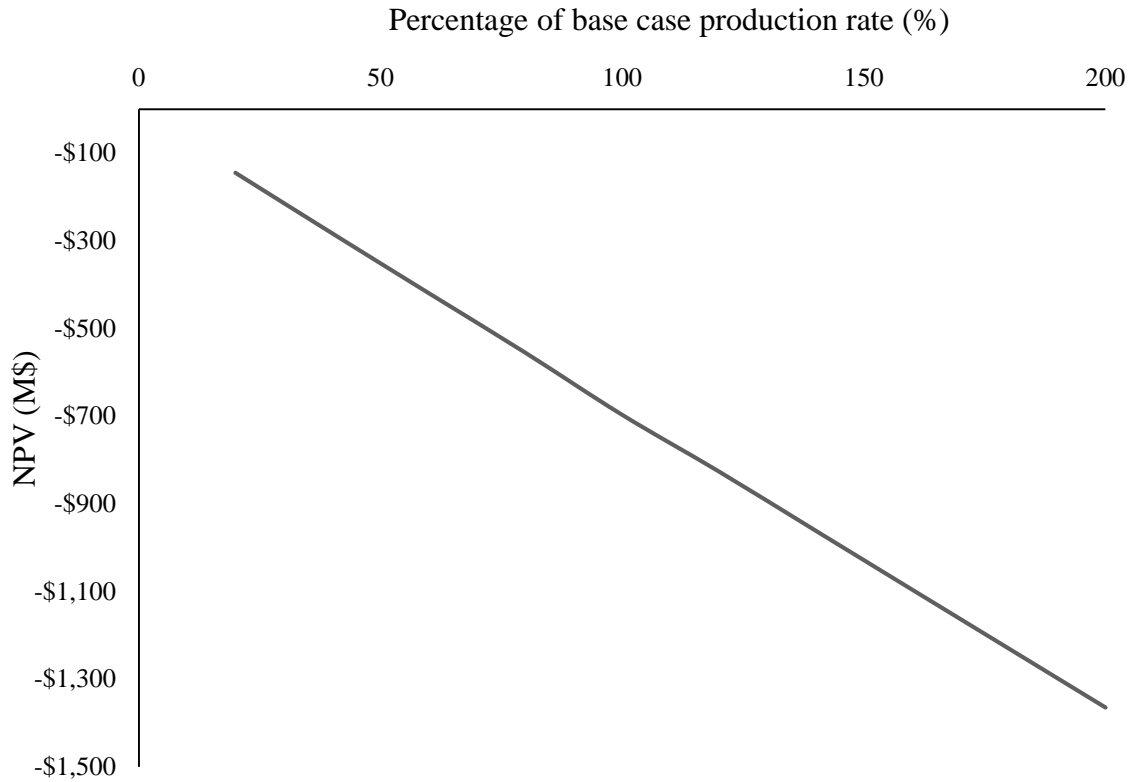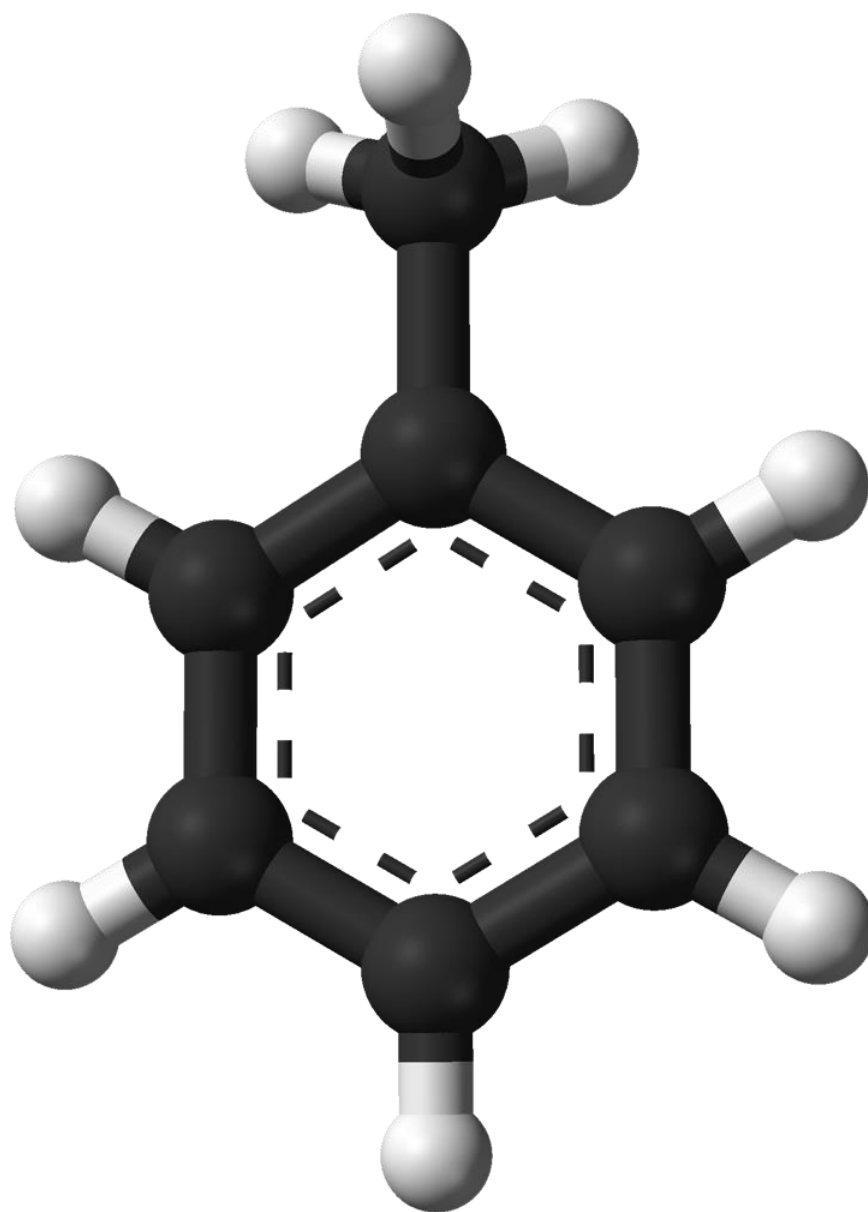
Percentage of base case production rate (%)

Figure 45– Effect of production capacity on NPV

CHAPTER 10
KEY ISSUES

The design of a toluene plant is a large and tremendous project. The time allowed for this kind of enterprise is usually of many years, and many engineers are required to complete the task. Due to time and staff limitations, some unresolved issues are still remaining. This chapter is dedicated to these issues.

10.1   Technical Issues

10.1.1   Section 100 - Feed Preparation and Reaction System

10.1.1.1   Reactor Unit

The design of the reactor unit is based on results coming from the reactor simulator. Nevertheless, simplifications were made in the development of this simulator. Therefore, the simulation results might differ from the actual behaviour of the system.

A major simplification that was made in the development of the reactor simulator concerned the heats of reaction, which were assumed to be constant and equivalent to the heats of reaction at 25°C. Therefore, the temperatures in the reactor and the heat needed for inter-stage heating are only blurred approximations.

The reactor simulator contains some limits and weaknesses, too. The compositions, temperatures and pressures are solved with an adaptive step size numerical method; the step size is constantly revised and decreased when the error from the step size is too large. The details of the design were presented in Chapter 3 and Appendix C. When the step size is decreased under a minimal size of 1.03×10^{-24}, the program stop solving and send an error message. Some systems of equations are therefore impossible to solve with the reactor simulator. Some reactor sizes and combinations could not be taken into consideration for the optimisation of the system. Better configurations could have lowered the capital cost of the reactor and the amount of catalyst used.

Furthermore, it was not possible to achieve high production volumes as a result of the limitation from the solver. The capital and operation costs were obtained from the simulation for final products flows of 537 kg/h for benzene, 1,093 kg/h for toluene and 547.2 kg/h for xylenes. The operation costs have been increased linearly with the production rate in order to obtain adjusted costs for a total production of 100,000 MT/yr. The capital costs have been adjusted using the 0.6 rule. The costing of the plant is therefore highly approximate.

10.1.1.2 Catalyst Regeneration

The catalyst regeneration system was not implemented in the simulation as the available version of UniSim did not provide tools for the continuous catalyst regeneration unit. The implementation of such a system to the simulation would make it more complete. It would as well permit to evaluate the cost associated with the regeneration of the system. These costs were not taken into account for the estimation of the capital and operating costs of the plant, nor for the economic evaluation of the project, leading to a big divergence from reality.

10.1.2 Section 300 - Light Hydrocarbons Recovery

The light hydrocarbons recovery section is made of a series of two distillation towers. The temperatures in the condensers of these towers are low; they are of -127.9°C for T-301 and -91.09°C for T-302. The pressures are of 120 kPa and 101.3 kPa. These conditions require large quantities of refrigerant at extremely low temperatures, leading to high operating costs. Corbetta *et al.* simulate the Cyclar process propane recovery from an hydrogen, methane and ethane stream with a distillation tower where a cut between ethane and propane is realized. The pressure and temperature of the condenser are of 20 bar and -74°C. At these operating conditions, the temperature of the refrigerant can be higher, and the price range is lower. This solution could be implemented to distillation towers T-301 and T-302 as an attempt to lower the operating cost of the plant. Nevertheless, the towers capital cost would increase due to the high pressure.

If more time had been available, another alternative design could have been implemented. In section 200, flash vessel V-201 operating conditions could have been modified to realize a cut between propane and ethylene, allowing the separation of the fuel gas from the reactor effluent stream and therefore removing the series of towers in this section. In section distillation tower could have been implemented between flash vessel V-201 and distillation tower T-301 to separate the aromatics from hydrocarbons C_3-C_8, cutting between benzene and octane on the base of volatilities. The C_3-C_8 stream, which consists of the unreacted propane and heavier hydrocarbons, could have been recycled and mixed with the feed of the reactor. The BTX stream would then go to distillation towers T-301 and T-302.

A final extension that could be added to the process is a hydrogen recovery system. It is possible to recover hydrogen by implementing an absorber/stripper system, a pressure swing adsorption

unit, a cold box, or a combination of these systems [19]. The choice of the recovery system would be based on the desired purity of the hydrogen product. The recovery of hydrogen would permit to sell it and increase the revenues.

10.2   Market Issues

The current market for petroleum industries is greatly suffering due to the decreasing price of oil barrels. This leads to a reduced resale value of the BTX products compared to the cost of the LPG feedstock. Therefore lowering the possible revenues. A solution to this would be to wait until the price of the oil barrel increases again. At this time, an economic feasibility analysis could be performed to determine if the plant would be profitable or not.

10.3   Economic Viability

The process design suggested to produce toluene requires many pieces of equipment, some of which are very complex, therefore increasing the fixed capital investment required to build this plant. Moreover, the cost of manufacturing to operate the plant is very high. Most of this cost originates from the cost of utilities, mainly because liquid nitrogen is required to condense the distillate of T-301, T-302 and T-401, as well as the cost of raw material. Since the revenues are minimal, it is not possible to recover the fixed capital investment and the manufacturing costs in order to be profitable. A solution to this would be to examine an alternative design, as suggested in Section 10.1.2, which would reduce both capital and operating costs.

CHAPTER 11
CONCLUSION AND RECOMMENDATIONS
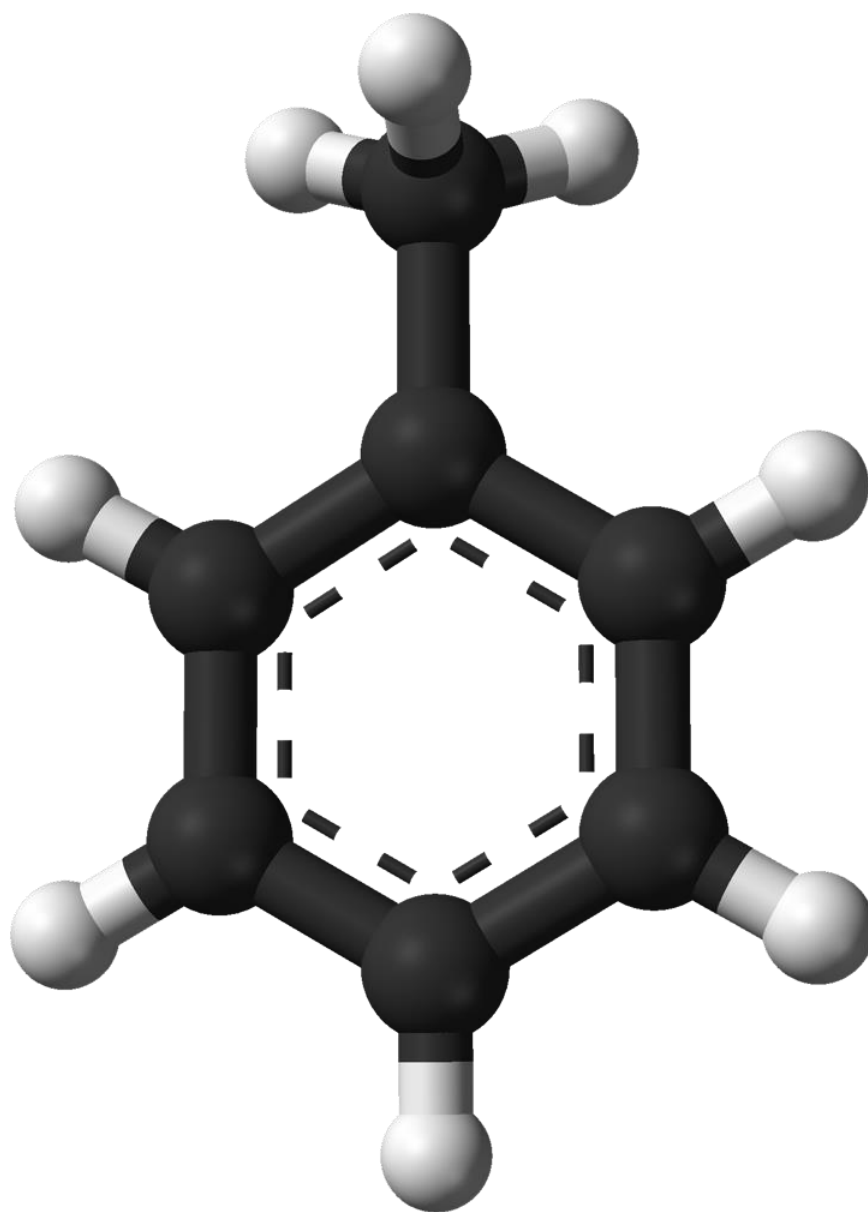
11.1 Conclusion

The goal of this project was to design a high-volume toluene production plant, with a capacity of 100,000 metric tons per year, and to simulate it using UniSim. Moreover, a profitability analysis was conducted to determine the economic viability of the plant.

Toluene is an aromatic hydrocarbon, which is commonly used in gasoline blending, in order to increase the octane rating of fuels. It is also very common in household products and is often used as a precursor in the chemical industry. Based on a marketplace analysis, it was concluded that the plant would be constructed in the United States, as it would be in close proximity to target markets and to raw materials, which are available at a competitive price.

Various synthesis pathways were examined, including naphtha reforming, methylation of benzene and aromatization processes from liquefied petroleum gases. The Cyclar process, an aromatization process, was selected based on the feedstock and its cost, the co-products synthesized as well as the reaction conditions and kinetics. However, this synthesis pathway is quite complex, as it is composed of 79 reactions and 19 compounds, which posed a challenge throughout the design process. Nonetheless, the process itself is quite simple, since the separation of hydrocarbons can easily be performed based on differences in relative volatilities.

The process was simulated in UniSim and thorough designs were completed for three major pieces of equipment: a heat exchanger, the reactor and a distillation column. After optimizing the process design, an economic and safety analysis were performed. It was estimated that the total grass root cost of the plant was $45.6M, and the corresponding manufacturing costs (without depreciation) were estimated to be $244M per year. For a BTX production rate of 100,000 metric tons per year, the revenues were estimated at $72.6M per year. Therefore, with a thorough profitability analysis, based on a ten-year project life, it was determined that the plant would not be profitable and therefore should not be built.

11.2 Recommendations

Some recommendations should be taken into consideration in order to examine different alternatives, in the hopes of being profitable and construct the plant.

An alternative design was suggested, which would allow to reduce both the capital and manufacturing costs. This process would use a different downstream separation sequence, therefore eliminating the need for a fourth distillation column.

Since a lot of hydrogen is produced as a by-product, an extension could be added to the plant to recover and sell it instead of using it as fuel gas, mixed with methane and ethane. This would greatly reduce the cost of waste treatment, since the flare load would be reduced.

Furthermore, since the catalyst life-span is only two years, it must be replaced five times during the project life, thus greatly increasing the cost of raw materials. To rectify this issue, a continuous catalyst regeneration cycle could be implemented, which would elongate the catalyst life duration.

Finally, the profitability analysis should be performed at a time when the market for petroleum products is at a higher value. This would increase the revenues from the resale of BTX products, thus possibly resulting in a positive net present value at the end of the project life.

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