



uOttawa

University of Ottawa

Chemical Engineering
Faculty of Engineering

Université d'Ottawa

Génie Chimique
Faculté de Génie

Synthesis of Toluene via Propane Dehydrocyclodimerization

Report 2 – Flowsheeting

Presented by Group 15

Katherine Bouchard	6788979
Karim François Charih	6131125
Roxanne Gauthier-Ferland	7032310
Eric Turriff	6793776

A report submitted to Dean Kennedy
in partial fulfillment of the requirements for the course of

Plant Design Project
CHG 4244

Department of Chemical and Biological Engineering
Faculty of Engineering
University of Ottawa
Submitted on Friday, February 12th, 2016

Executive Summary

The high-volume aromatics production plant proposed in this work is a variant of the Cyclar process developed conjointly by BP and UOP. A process synthesis analysis led to the elaboration of a preliminary flowsheet for the plant. The plant consists of four main sections: a feed preparation and reactor section, a reactor effluent separation section, a light ends separation section and an aromatics separation section. With a propane feed of 1442 kg/h, the plant produces 171.7 kg/h of toluene, 94.5 kg/h of benzene and 87.12 kg/h with a single pass, along with fuel gas and hydrogen. The apparent single-pass conversion of propane is 54%.

A revised reaction scheme consisting of 79 reactions was considered for process simulation purposes. An initial simulation was performed with the Honeywell UniSim software using the Peng-Robinson equation of state and the Glycol package, based on the nature of the species involved. The process could not be modeled completely, as UniSim could not solve for the reactor effluent composition and properties. The lack of a working reactor is a severely limiting bottleneck in the development and optimization of the overall process, as a recycle stream cannot be implemented. Possible and realistic solutions to this problem are currently being explored.

A separation strategy was devised based on data published by Harris *et al.* for the composition of the reactor effluent stream for a single-pass of propane over a Ga-HZSM5 catalyst. The reactor operating conditions proposed by Harris *et al.* and implemented in the simulation are 520°C and 400 kPa. The separation strategy developed takes advantage of the ideality of the hydrocarbon mixture to make use of a flash vessel, five distillation columns and an absorption column.

Control strategies for the principal units are presented in order to control important conditions such as flowrate, pressure and temperature.

Finally, a preliminary list of utilities is presented, although duties cannot be accurately estimated at this moment.

Table of Contents

Executive Summary	i
List of Figures	iv
List of Tables	v
Nomenclature	vi
CHAPTER 2 - PROCESS DESCRIPTION	
2.1. Process Selection	1
2.2. Process Overview.....	2
2.2.1. Raw Materials and Preliminary Cost Estimation.....	2
2.2.2. By-Products and Co-Products.....	4
2.2.3. Reaction Conditions and Kinetics.....	6
2.2.3.1. Reaction Spontaneity	6
2.2.3.2. Reaction Catalysis and Kinetics.....	8
2.2.4. Block Flow Diagram.....	8
2.2.5. Overall Plant Material Balance	11
2.3. Detailed Design Description	11
2.3.1. Feed Preparation and Reactor System	11
2.3.2. Reactor Effluent Separation Process.....	13
2.3.3. Light Ends Recovery.....	15
2.3.4. Aromatics Separation.....	18
2.4. Process Control Strategy.....	20
2.4.1. Control in the Feed Preparation Section	20
2.4.2. Control in the Reactor Section.....	21
2.4.3. Control of Downstream Separation Section	21
CHAPTER 3 - PROCESS AND EQUIPMENT DESIGN	
3.1. Feed Preparation	22
3.2. Reaction System.....	22
3.2.1. Reactor	22
3.2.2. Catalyst Regeneration	24
3.3. Separation Processes.....	25

3.3.1.	Flash Separation.....	26
3.3.2.	Propane, Hydrogen and Fuel Gas Recovery	26
3.3.3.	Benzene, Toluene and Xylenes Recovery	27
3.3.3.1.	BTX Separation Tower	27
3.3.3.2.	Benzene Distillation Tower	28
3.3.3.3.	Toluene Distillation Tower	28
3.4.	Thermodynamic Fluid Package Selection	28
CHAPTER 4 - MISCELLANEOUS STUDIES		
4.1.	Optimization of Equipment.....	30
CHAPTER 5 - OUTSIDE BATTERY LIMIT		
5.1.	Preliminary List of Utilities	31
Appendix G - Sample Calculations and Governing Equations..... 36		
	Thermodynamic Analysis	36
	Mass Balance	38
	Preliminary Economic Analysis	40
	Reaction Kinetics.....	41
Appendix D – Simulation Summaries 44		
Appendix J – Ethics Agreement and Task Allocation Sheet 46		

List of Figures

Figure 1 – Comparison of the ethylene margins using LPG and naphtha as feedstock for the first 2015 quarter [3].....	1
Figure 2 – Price of propane in North America and Saudi Arabia over the 2013-2015 period. (Generated from published prices [10], [15])	3
Figure 3 – Dehydrocyclodimerization of propane on a zeolite catalyst [18].....	4
Figure 4 – Dependence of Gibbs free energy on temperature	7
Figure 5 – Block flow diagram of the toluene production process.....	10
Figure 6 – PFD 100 (Feed Preparation and Reactor System).....	12
Figure 7 – PFD 200 (Reactor Effluent Separation)	14
Figure 8 – PFD 300 (Light Ends Separation)	16
Figure 9 – PFD 400 (Aromatics Separation)	19
Figure 10 – Catalyst continuous regeneration system (adapted from [7]).....	25
Figure 11 – Pilot plant conversion of propane as a first order irreversible reaction [32]	43

List of Tables

Table 1 – Preliminary mass flows, prices and cash flows for the propane aromatization process [2], [16], [17].....	4
Table 2 – Distribution of the products of the aromatization of propane over a Ga-doped HZSM-5 catalyst adapted from Harris <i>et al.</i> [19]	5
Table 3 – Overall material balance from single pass	11
Table 4 – Stream table for Section 100 (Feed Preparation and Reactor System).....	12
Table 5 - Stream table for Section 200 (Reactor Effluent Separation).....	14
Table 6 - Stream table for Section 300 (Light Ends Separation).....	17
Table 7 – Stream table for Section 400 (Aromatics separation).....	19
Table 8 – Preliminary list of case studies to be performed around the main process units	30
Table 9 – Preliminary list of utilities	31
Table 10 – Thermodynamic properties of propane and toluene at standard conditions	37
Table 11 – Product mass distribution.....	38
Table 12 – Weight distribution of aromatics	39
Table 13 – Overall mass balance on the basis of 120,000 MT of propane per year.....	40
Table 14 – Costs of main components.....	41
Table 15 – Distillation tower specifications	44
Table 16 – Compositions of chemicals in the absorption tower	44
Table 17 - Compositions of chemicals in the flash vessel	45

Nomenclature

Abbreviations

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

Equipment Labels

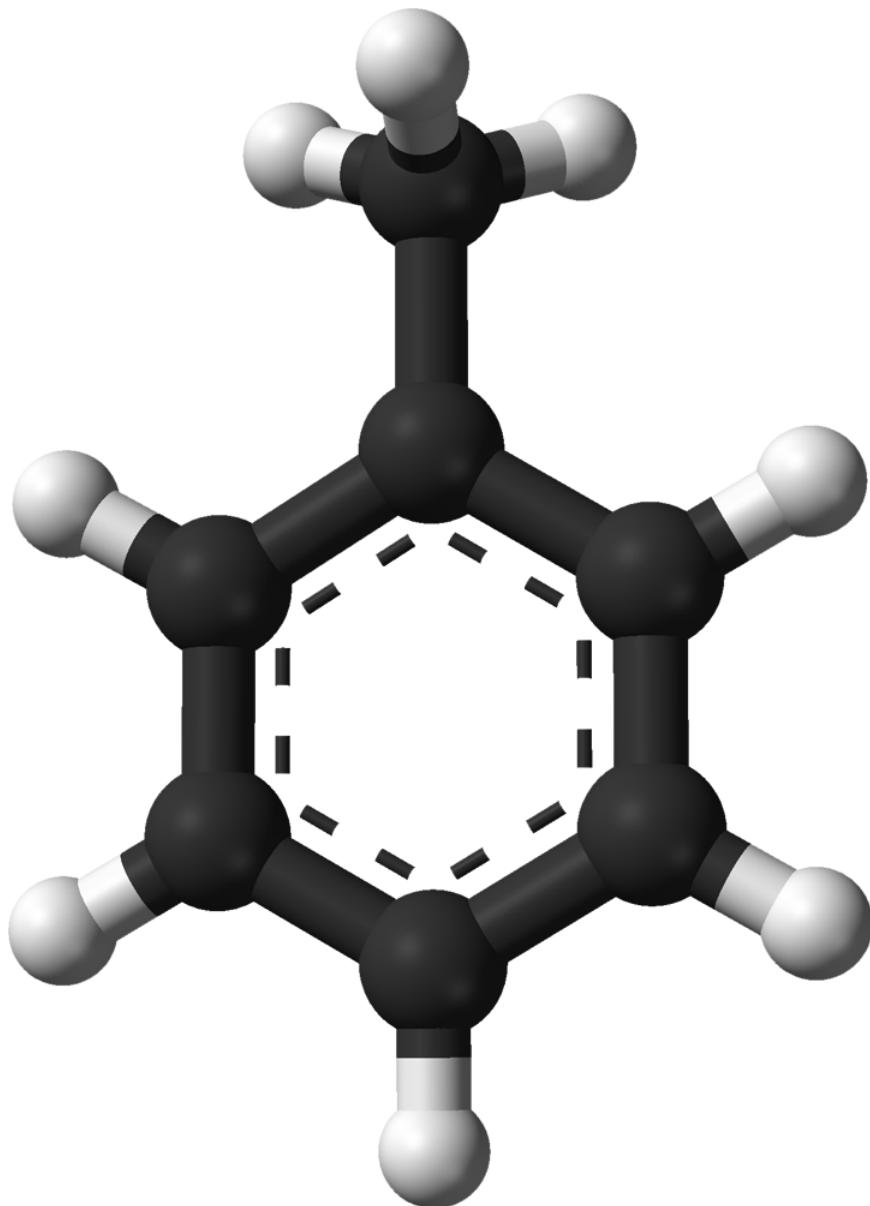
HX	Heat Exchanger (including fired heaters)
MX	Mixer
P	Pump
R	Reactor
RG	Regenerator
T	Tower
V	Vessel
VL	Valve

Symbols

E_a	Activation Energy (J/mol)
A_0	Pre-exponential Factor (mol/kg catalyst h Pa or mol/kg catalyst h Pa ²)
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)
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)

CHAPTER 2

PROCESS DESCRIPTION



2.1. Process Selection

The most common route for producing toluene and other petrochemical-grade aromatics remains the conventional catalytic reforming process from naphtha [1]. 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.

The cost of raw materials is pivotal in determining if a process is economically viable or not [2], since 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 [3]. Figure 1 illustrates the ethylene profit margins over the first quarter of 2015.

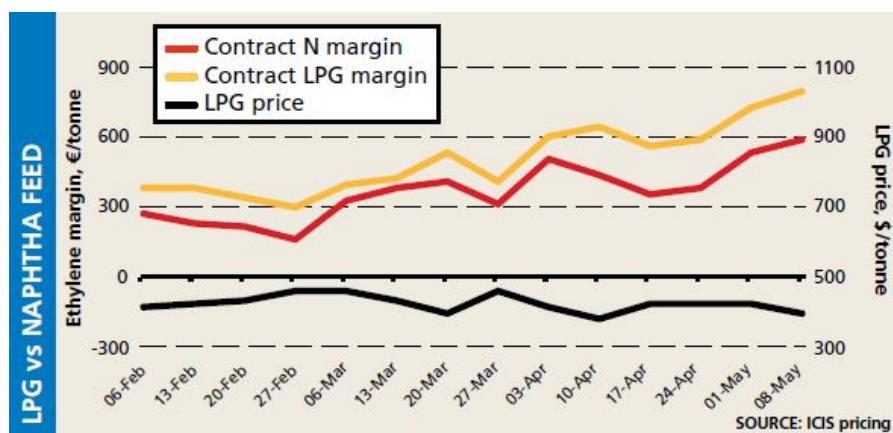


Figure 1 – Comparison of the ethylene margins using LPG and naphtha as feedstock for the first 2015 quarter [3]

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 [4], although the price of naphtha has momentarily gained momentum for a short period in 2015 [5]. 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 [6]. 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 [7]. Furthermore, the Cyclar process also regenerates the catalyst continuously with its CCR technology, bypassing the need for alternating reactors seen in all other technologies.

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 [8].

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 [9]. Kinetics data for the other LPG aromatization processes is not readily available.

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.

2.2. Process Overview

2.2.1. Raw Materials and Preliminary Cost Estimation

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. It will be later possible to reassess this decision if more data becomes available, as the process can operate using both chemicals as raw materials. Even though butanes

achieve slightly higher yields (66% versus 62%) [7], it is worth noting that propane is generally less costly than butane [10] 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 [11].

Propane feedstock is available at relatively high purities. The propane supplied by Saudi Aramco is at least 95% pure [12]. The remaining 5% consists of butanes (4%) and olefins (alkenes). This feedstock can be, 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 [7]. The Canadian supplier Superior Propane provides propane with a similar composition [13], suggesting that high purity propane is readily available in these two regions.

In Saudi Arabia, the price of propane has been following a decreasing trend over the last three years (2013-2015) as shown in Figure 2, 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 [14] and closed at 205 USD per metric ton in December 2015 [15].



Figure 2 – Price of propane in North America and Saudi Arabia over the 2013-2015 period. (Generated from published prices [10], [15])

When assessing the viability of a process, a simple economic analysis is conducted to have a simple estimation of profits. The estimation of profits is calculated by Equation 2-1:

$$Profitability = \sum_i^{products} C_i \times \dot{m}_i - \sum_j^{raw materials} C_j \times \dot{m}_j \quad \text{Equation 2-1}$$

However, to conduct the profitability analysis a preliminary 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 1.

Table 1 – Preliminary mass flows, prices and cash flows for the propane aromatization process [2], [16], [17]

Compound	Mass Input (MT/yr)	Mass Output (MT/yr)	Chemical Price (USD/MT)	Cash flow (USD/yr)
Propane	1.20x10 ⁵	120	345	-4.14x10 ⁷
Toluene	-	3.10x10 ⁴	669	2.08x10 ⁷
Benzene	-	2.42x10 ⁴	740	1.79x10 ⁷
Xylene	-	1.42x10 ⁴	825	1.17x10 ⁷
Heavy Aromatics (C ₉ +)	-	6.12x10 ³	N/A	N/A
Fuel gas	-	3.72x10 ⁴	N/A	N/A
Hydrogen	-	7.08x10 ³	1280	9.06x10 ⁶
Total	1.20x10⁵	1.20x10⁵	N/A	1.81x10⁷

From Table 1, it can be concluded that with a propane feed of 1.20x10⁵ MT/yr, only 120 MT/yr is unreacted, which signifies the propane has a conversion of 99%. In addition, a cash flow of 18 million dollars is calculated from the aromatization of the propane. The preliminary analysis of the process leads to the conclusion that it may be economically viable.

2.2.2. By-Products and Co-Products

The Cyclar process is often described as a “dehydrocyclodimerization” reaction [7] and consists of a reaction network which leads to the formation of numerous co-products and by-products as seen in Figure 3.



Figure 3 – Dehydrocyclodimerization of propane on a zeolite catalyst [18]

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 [18].

As the propene intermediate accumulates on the catalyst, it oligomerizes to form longer alkenes which may take two routes [18]. 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 [18]. 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 [7]. Other by-products (ethylene, butene, C₄-C₆ alkanes, ethylbenzene, naphthalenes) are formed in relatively small amounts corresponding to roughly 5% of the total product (for a single pass). The single-pass yields for all products of the aromatization of propane over a Ga-ZSM-5 zeolite at 520°C and 400 kPa is tabulated in Table 2.

Table 2 – Distribution of the products of the aromatization of propane over a Ga-doped HZSM-5 catalyst adapted from Harris *et al.*[19]

Component	Feed (wt %)	Product (wt %)
Hydrogen	-	2.22
Methane	-	10.1
Ethane	-	8.54
Propane	100.0	54.0
Toluene	-	11.8
Benzene	-	7.34
Xylenes	-	6.01

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 [20].

The fuel gas generated via cracking contains 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.

A preliminary mass balance based on experimental yields is presented in Appendix G - Sample Calculations and Governing Equations. The profits generated through sales of toluene and the by-products represent roughly 18M USD/yr assuming a 120,000 ton/year propane feed.

2.2.3. 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.

2.2.3.1. 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 2-2:

$$\Delta G_f^o_{298} = \sum_i^{n \text{ products}} a_i \Delta G_{f,i}^o_{298} - \sum_j^{n \text{ reactants}} a_j \Delta G_{f,j}^o_{298} \quad \text{Equation 2-2}$$

Where a_x is the stoichiometric coefficient of species X and $\Delta G_{x,f}^o_{298}$ 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 2-3). This equilibrium constant can be used in conjunction with Equation 2-4 to find the change in Gibbs free energy at temperature 2:

$$K_2 = e^{\frac{-\Delta H_f^o_{298}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad \text{Equation 2-3}$$

$$\Delta G^T = -RT \ln(K_2) \quad \text{Equation 2-4}$$

From Equation 2-3, 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 [19]. The propane dehydrogenation can be described by the following chemical reaction [9]:

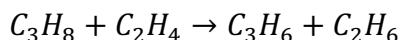


Figure 4 depicts the reaction spontaneity as a function of reaction temperature.

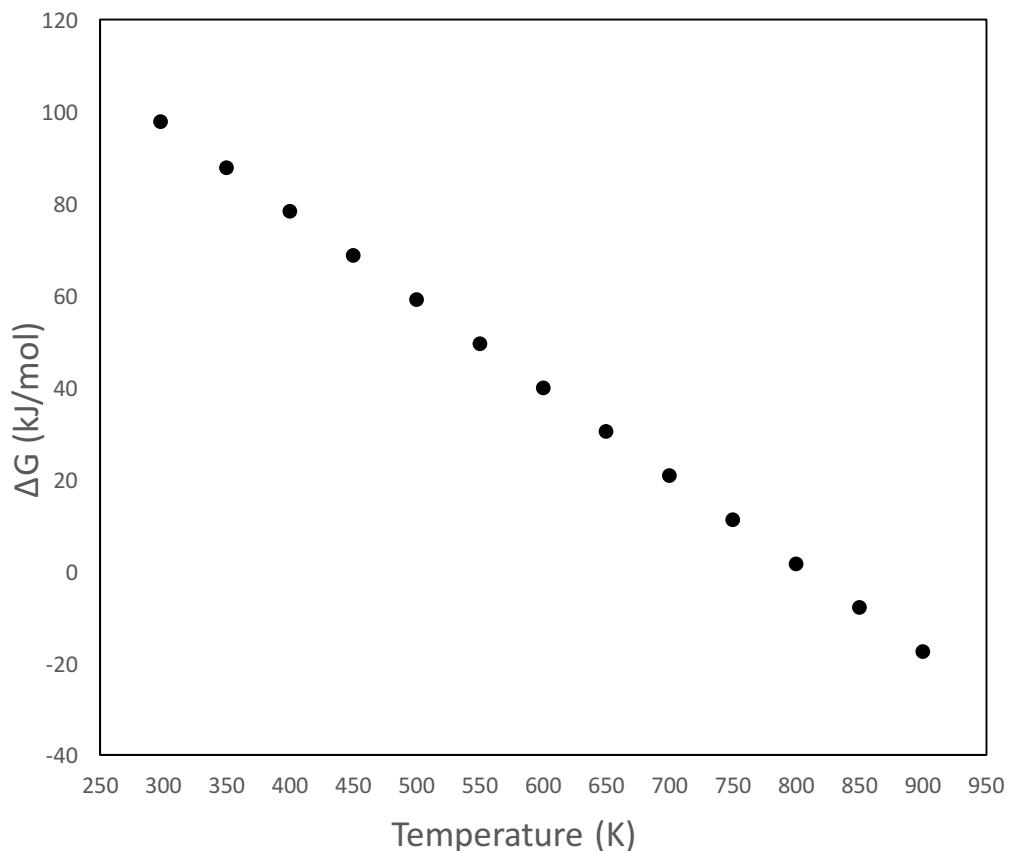


Figure 4 – Dependence of Gibbs free energy on temperature

Figure 4 shows 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 at room temperature.

However as the temperature increases, so does the spontaneity. Therefore, the production of toluene can be considered plausible at room temperature.

2.2.3.2. Reaction Catalysis and Kinetics

The Cyclar process described by Harris *et al.* uses a gallium loaded catalyst: ZSM-5 (Ga-ZSM-5) [19]. ZSM-5 is a medium pore zeolite used in the aromatization of alkanes [21]. This catalyst is widely used due to its pore size as well as the low acid site density, which greatly reduces the catalyst deactivation from coking [21]. This zeolite is loaded with gallium in order to increase the conversion as well as the selectivity of aromatics [19]. In addition, the lifetime of Ga-ZSM-5 is expected to be two years using available CCR technology [21]. Corbetta *et al.* [9] studied the kinetics of the aromatization of propane with H-ZSM-5, the protonated form of ZSM-5. The reactor system is modeled an isothermal pseudo-homogeneous packed bed reactor. The reaction rates can be simplified to Equation 4, assuming that the adsorption and desorption steps are not the rate-limiting steps [9]:

$$r_j = k_j \prod_{m=1}^n P_m \quad \text{Equation 2-5}$$

The kinetic constants for all 79 reactions were modeled as the Arrhenius expression, described by Equation 2-6:

$$k_j = A_0 e^{\frac{-E_a}{RT}} \quad \text{Equation 2-6}$$

The full list of the pre-exponential factor and the activation energy for every reaction is found in Appendix G - Sample Calculations and Governing Equations.

2.2.4. Block Flow Diagram

While a complete description of the process and its operating conditions will follow in Chapter 3, the block flow diagram of the process is presented in Figure 5 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 a BTX liquid stream exits from the bottom. The gas stream, containing mainly hydrogen, propane and fuel gas is sent to a triethylene glycol (TEG) absorber to separate remaining BTX. These aromatics are recovered in a TEG regeneration tower and then mixed with the flash vessel exit BTX stream.

The gas stream exiting the absorber is sent to a distillation tower to recover propane. The propane is recycled back into the feed preparation stream, where it is mixed with the fresh propane stream. The combined BTX stream is further purified from remaining light hydrocarbons in a distillation tower. The BTX stream is then processed in a series of distillation columns, in which the benzene, toluene and xylenes are separated.

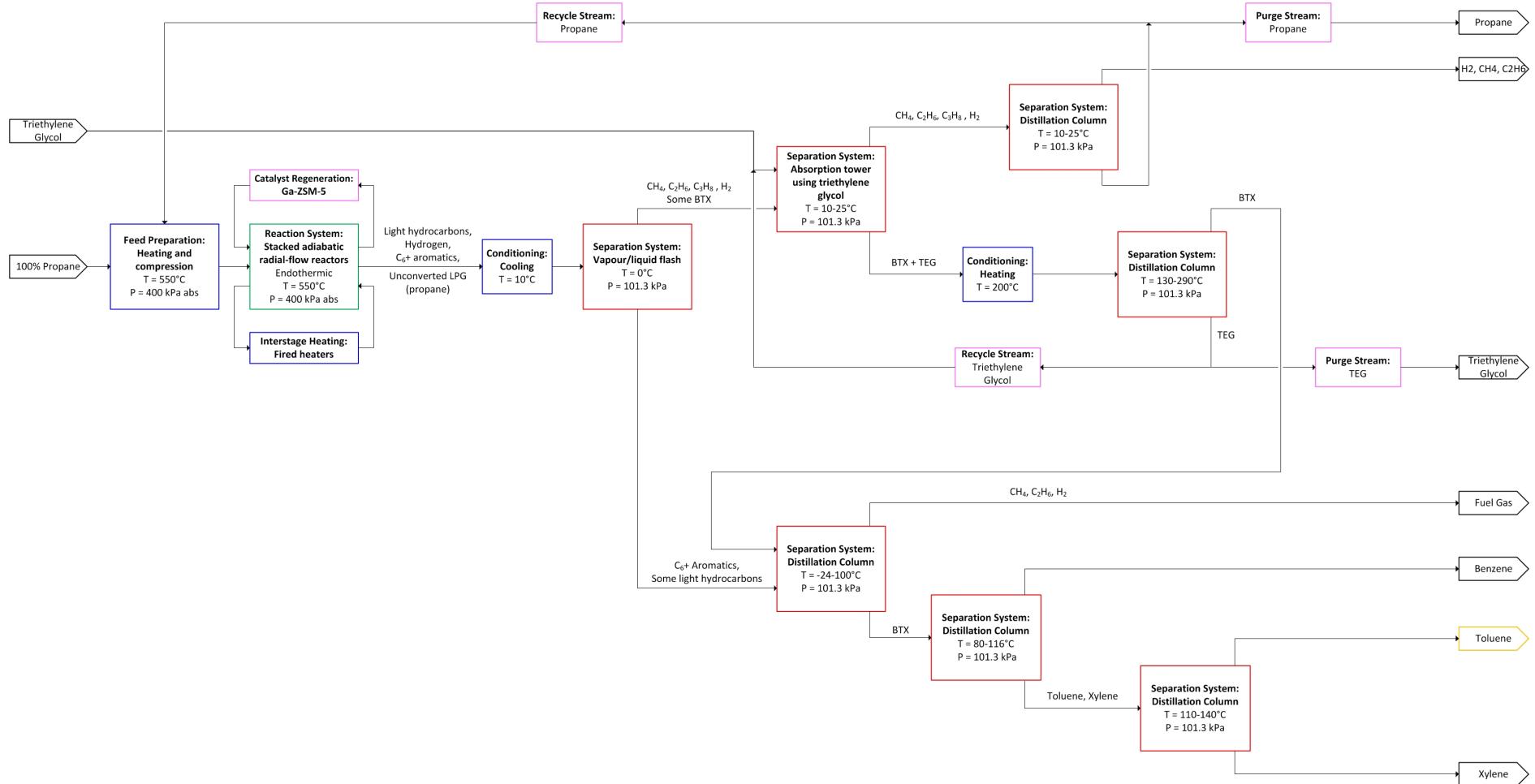


Figure 5 – Block flow diagram of the toluene production process

2.2.5. Overall Plant Material Balance

An overall plant material balance was generated by means of a UniSim simulation. Due to difficulties simulating the reactor system, only a single pass product distribution from literature was considered [19]. The overall material balance for a single pass can be found in Table 3.

Table 3 – Overall material balance from single pass

Compound	Inlet Mass Flow Rate (kg/h)	Outlet Mass Flow Rate (kg/h)
Toluene	-	171.7
Benzene	-	94.5
Xylenes	-	87.12
Propane	1442	781.2
Ethane	-	122.8
Methane	-	145.3
Hydrogen	-	31.4
TEG	100	100

From Table 3, it can be seen that, for a single pass, 661 kg of propane is consumed per hour. The production rate of toluene is 171.7 kg/hr. The production of toluene can be increased with the implementation of a recycle stream for the unreacted propane. Recycling the propane would be feasible since more than half of the propane fed into the system is unreacted. The ethane, methane and hydrogen outlet flow may be revisited in the future as these compounds may be used for heat integration purposes.

2.3. Detailed Design Description

2.3.1. Feed Preparation and Reactor System

The process flow diagram of the feed preparation and reaction system (PFD 100) is presented in Figure 6. The feed mixed with recycle streams from Sections 300 and 400 (PFD 300 and PFD 400) is depressurized through valve VL-101 and heated to the reactor temperature in heat exchanger HX-101 and fired heater HX-102. It is then sent to the stacked reactors, which are represented by the reactor R-101. The reactor operates at 520°C and 400 kPa. A continuous catalyst regeneration (CCR) system, RG-101, operates alongside the reactor.

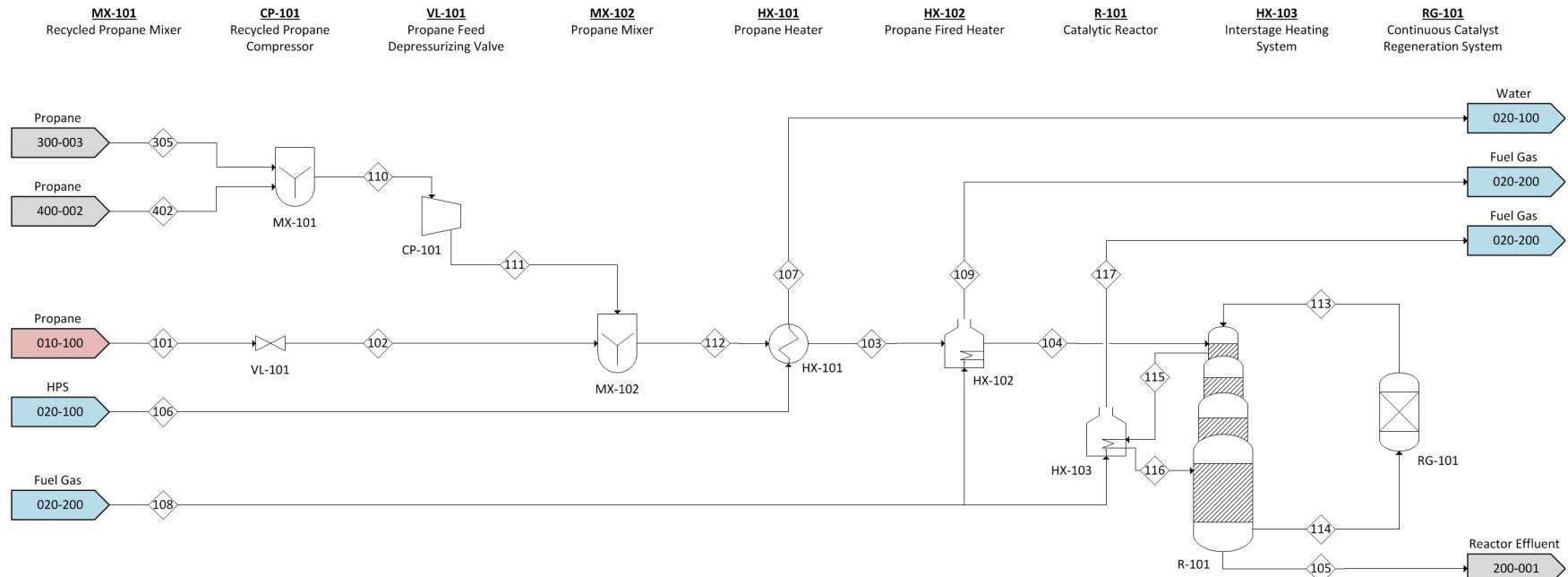


Figure 6 – PFD 100 (Feed Preparation and Reactor System)

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

Stream	Mass Flow Rate (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction									
					Benzene	p-Xylene	m-Xylene	o-Xylene	Methane	Ethane	Propane	Hydrogen	Toluene	TEG
101	1442.0	25.0	952.3	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
102	1442.0	-3.9	420.0	0.20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
103	1442.0	250.0	410.0	1.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
104	1442.0	550.0	400.0	1.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
105	1442.1	550.0	400.0	1.00	0.0734	0.0235	0.0235	0.0131	0.1008	0.0854	0.5400	0.0219	0.1183	0.0000

2.3.2. Reactor Effluent Separation Process

The process flow diagram for the preliminary separation process (PFD 200) is presented in

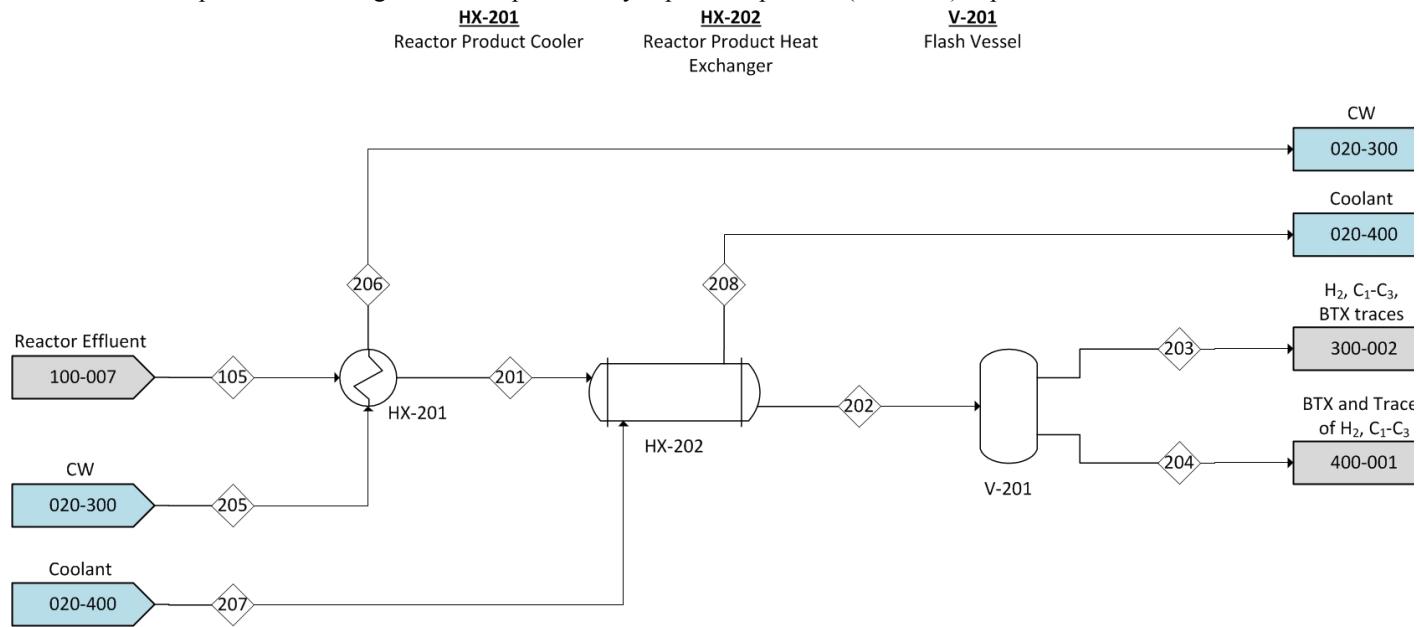


Figure 7. The reactor effluent is cooled down in heat exchangers HX-201 and HX-202 before being sent to the flash vessel V-201, where C_6 and heavier aromatics are liquefied while most light hydrocarbons (such as ethane and methane), hydrogen and unconverted LPG remain in the vapour phase. The operating conditions of the flash vessel V-201 are 101.3 kPa and 0°C, in order to achieve a proper separation.

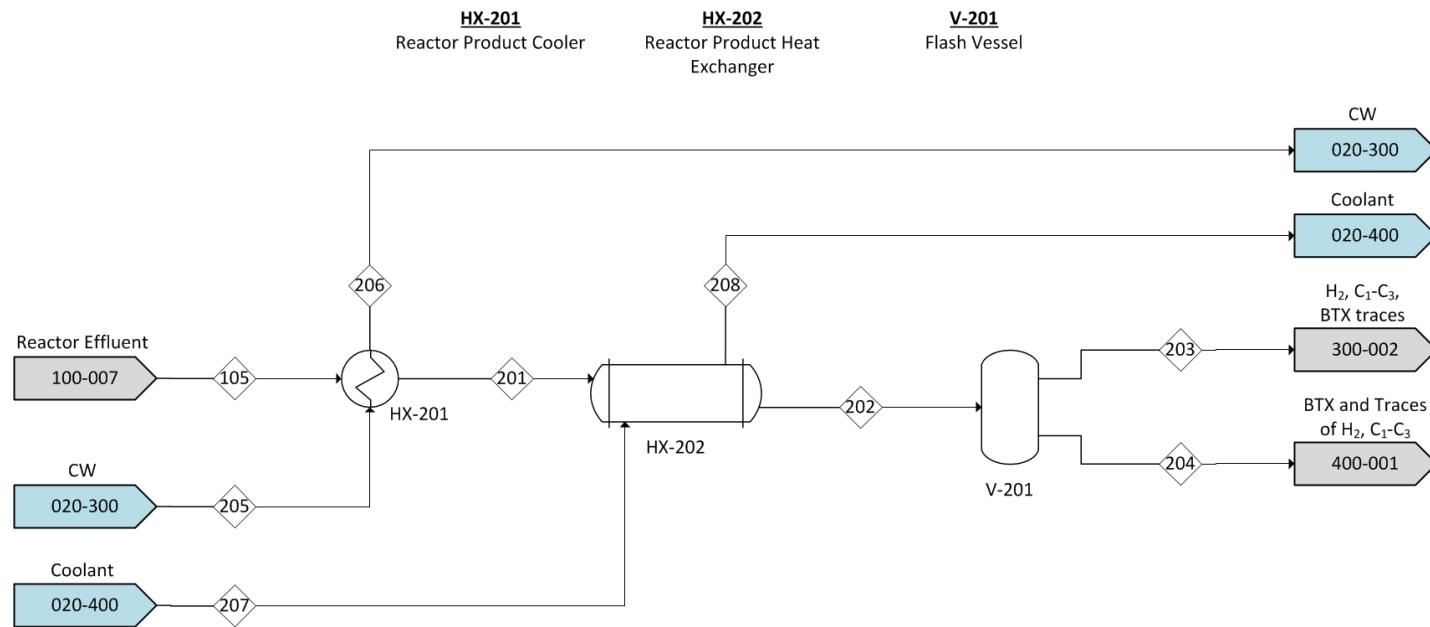


Figure 7 – PFD 200 (Reactor Effluent Separation)

Table 5 - Stream table for Section 200 (Reactor Effluent Separation)

Stream	Mass Flow Rate (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction									
					Benzene	p-Xylene	m-Xylene	o-Xylene	Methane	Ethane	Propane	Hydrogen	Toluene	TEG
201	1442.1	45.0	390.0	0.95	0.0734	0.0235	0.0235	0.0131	0.1008	0.0854	0.5400	0.0219	0.1183	0.0000
202	1442.1	10.0	380.0	0.91	0.0734	0.0235	0.0235	0.0131	0.1008	0.0854	0.5400	0.0219	0.1183	0.0000
203	1134.2	0.4	101.3	1.00	0.0338	0.0010	0.0010	0.0005	0.1281	0.1084	0.6801	0.0279	0.0193	0.0000
204	307.9	0.4	101.3	0.00	0.2193	0.1065	0.1065	0.0597	0.0001	0.0009	0.0238	0.0000	0.4831	0.0000

2.3.3. Light Ends Recovery

The process flow diagram of propane purification (PFD 300) is presented in Figure 8. The gas stream from Section 200 goes into absorber T-301, where the remaining BTX is absorbed in triethylene glycol (TEG). The BTX is recovered in the liquid phase of the TEG regeneration distillation tower T-303. The TEG is recycled to the absorber T-301 while the BTX stream is sent to the BTX recovery section (Section 400). A purge stream is added for the TEG, to ensure there is no accumulation in the system. The unconverted propane is recovered from the hydrogen-rich stream in distillation tower T-302, and is mixed with the fresh propane feed of the process. The distillation towers T-302 and T-303 operate at atmospheric pressure.

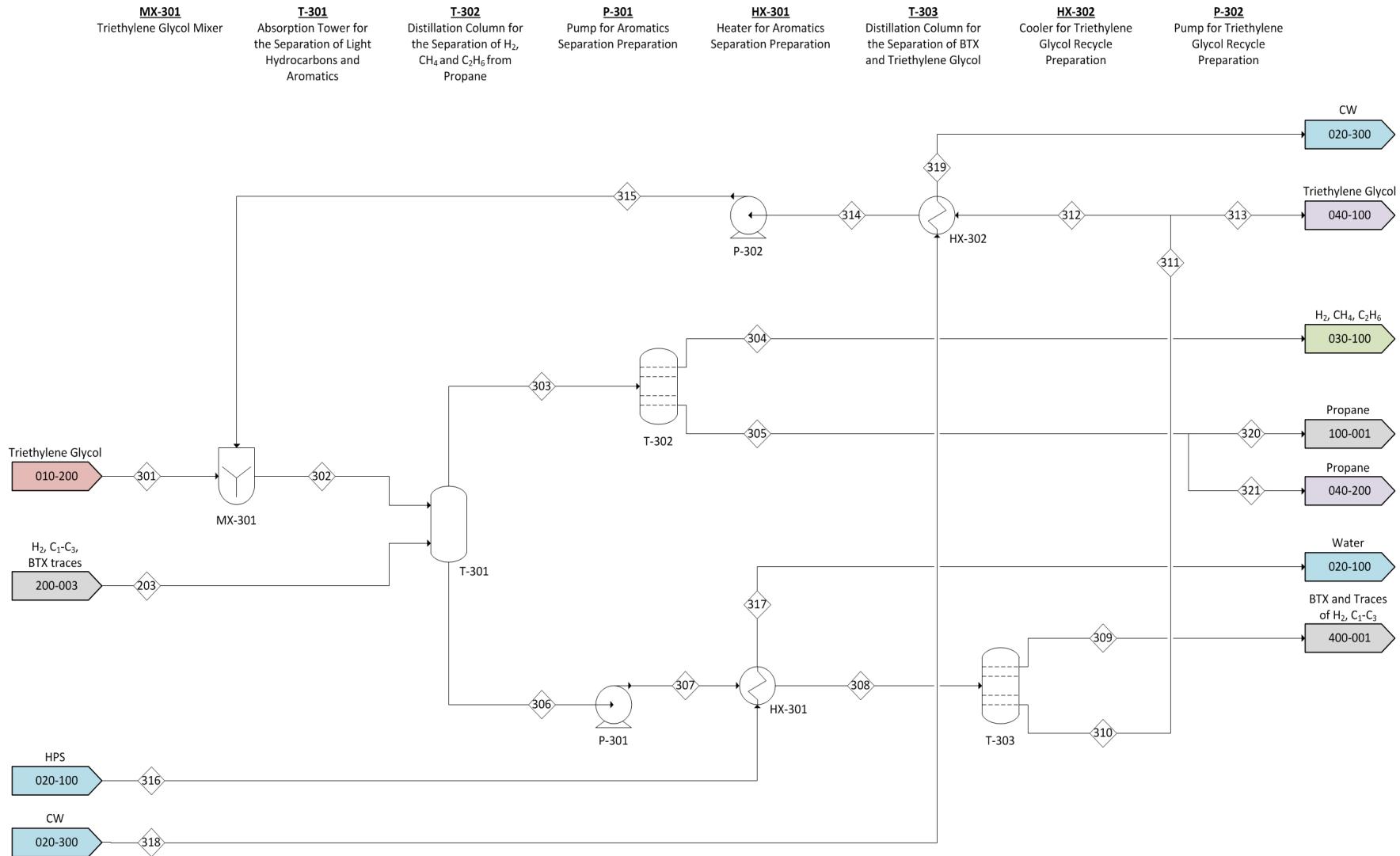


Figure 8 – PFD 300 (Light Ends Separation)

Table 6 - Stream table for Section 300 (Light Ends Separation)

Stream	Mass Flow Rate (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction									
					Benzene	p-Xylene	m-Xylene	o-Xylene	Methane	Ethane	Propane	Hydrogen	Toluene	TEG
301	100.0	25.0	101.3	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
302	990.8	25.0	101.3	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.9999
303	1081.0	25.2	101.3	1.00	0.0097	0.0000	0.0000	0.0000	0.1344	0.1137	0.7129	0.0292	0.0001	0.0000
304	299.8	-118.5	101.3	1.00	0.0000	0.0000	0.0000	0.0000	0.4845	0.4097	0.0004	0.1053	0.0000	0.0000
305	781.2	-42.0	101.3	0.00	0.0134	0.0000	0.0000	0.0000	0.0000	0.0001	0.9864	0.0000	0.0002	0.0000
306	1043.9	6.2	101.3	0.00	0.0267	0.0011	0.0011	0.0005	0.0000	0.0000	0.0006	0.0000	0.0208	0.9490
307	1043.9	6.2	151.3	0.00	0.0267	0.0011	0.0011	0.0005	0.0000	0.0000	0.0006	0.0000	0.0208	0.9490
308	1043.9	200.0	101.3	0.07	0.0267	0.0011	0.0011	0.0005	0.0000	0.0000	0.0006	0.0000	0.0208	0.9490
309	53.8	130.6	101.3	1.00	0.5182	0.0218	0.0214	0.0104	0.0002	0.0008	0.0125	0.0001	0.4038	0.0108
310	990.2	287.3	101.3	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.9999
311	989.7	287.3	101.3	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.9999
312	890.8	287.3	101.3	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.9999
313	99.0	287.3	101.3	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.9999
314	890.8	25.0	91.3	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.9999
315	890.8	25.0	101.3	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.9999

2.3.4. Aromatics Separation

The process flow diagram for the BTX recovery process (PFD 400) is presented in Figure 9. The combined BTX stream from Section 200 and Section 300 go to a first distillation tower, T-401, to purify the stream from remaining propane, which is recycled to the entry of the process (PFD 100). Tower T-401 allows to recover benzene as a distillate, while the remaining aromatics are sent to the second distillation tower, T-403, to separate toluene and xylenes. Both distillation towers operate at atmospheric pressure.

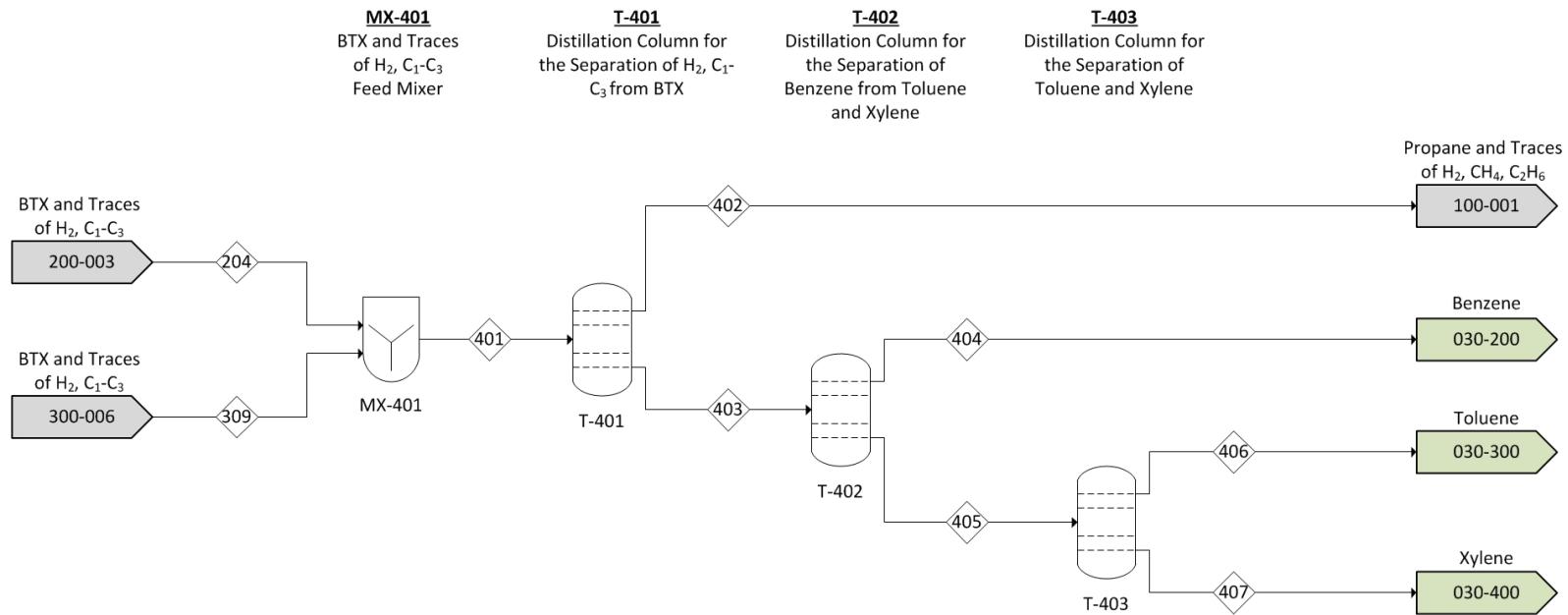


Figure 9 – PFD 400 (Aromatics Separation)

Table 7 – Stream table for Section 400 (Aromatics separation)

Stream	Mass Flow Rate (kg/h)	Temperature (°C)	Pressure (kPa)	Vapour Fraction	Mass Fraction									
					Benzene	p-Xylene	m-Xylene	o-Xylene	Methane	Ethane	Propane	Hydrogen	Toluene	TEG
401	361.7	51.6	101.3	0.02	0.2637	0.0939	0.0939	0.0524	0.0001	0.0009	0.0222	0.0000	0.4713	0.0016
402	8.3	-23.7	101.3	1.00	0.0092	0.0000	0.0000	0.0000	0.0056	0.0389	0.9446	0.0007	0.0010	0.0000
403	353.4	99.5	101.3	0.00	0.2697	0.0961	0.0961	0.0536	0.0000	0.0000	0.0005	0.0000	0.4823	0.0016
404	94.5	80.5	101.3	1.00	0.9864	0.0000	0.0000	0.0000	0.0000	0.0000	0.0018	0.0000	0.0118	0.0000
405	258.9	116.7	101.3	0.00	0.0081	0.1312	0.1312	0.0732	0.0000	0.0000	0.0000	0.0000	0.6541	0.0022
406	171.7	110.1	101.3	1.00	0.0122	0.0012	0.0010	0.0001	0.0000	0.0000	0.0000	0.0000	0.9855	0.0001
407	87.1	139.9	101.3	0.00	0.0000	0.3875	0.3877	0.2174	0.0000	0.0000	0.0000	0.0000	0.0009	0.0065

2.4. 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.

2.4.1. 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 flow control valve placed upstream of the process allows for flexibility and/or consistency in terms of capacity.

The feed preparation section (PFD 100) of the plant includes a fired heater (HX-102). This unit immediately precedes the reactor (R-101 in PFD 100), 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 HX-102 is justified.

The heating of propane in HX-102 relies on the combustion of fuel gas (a methane-ethane mixture), 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-201 measured with a temperature element is sent to a controller, which can vary the flow rate of fuel gas provided to HX-102, in order to counteract disturbances or change the operating temperature in R-101.

2.4.2. 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-201 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 in the fired heater (HX-103) coupled to R-101. The flowrate of the fuel gas provided to HX-103 can be controlled in order to ensure that every interstage stream is returned to the following reactor stage at the proper temperature. The temperature is to be monitored after each stage, in order to maintain high reaction rates.

The pressure is also to be monitored such that the reactor effluent remains slightly over atmospheric pressure, as the aromatics yield is higher at low pressures [7]. The pressure is adjusted through the aperture of a valve located upstream.

2.4.3. Control of Downstream Separation Section

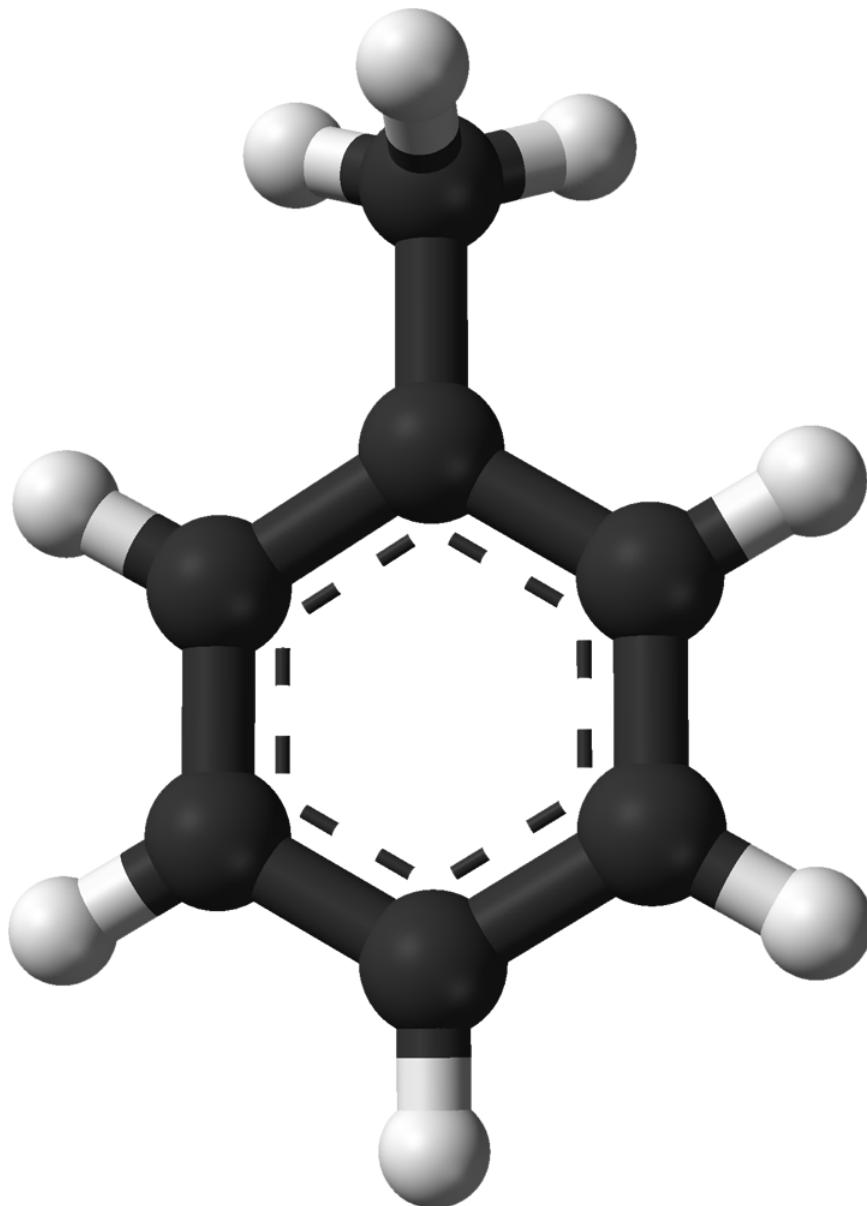
The downstream plant section where product separation is performed comprises many units around which control strategies must be implemented. The flash vessel (V-201) designed to separate the heavy products (mainly aromatics) from the light products (mainly light hydrocarbons and hydrogen) encloses a 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 element controlling the rotation speed of a pump 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 distillation columns are controlled by varying the flow rate of cooling water and steam in the condenser and reboiler, respectively. The level of liquids is controlled with pumps located downstream, which can respond to a change in the level of liquid.

All critical temperature changes in process streams done in heat exchangers can be controlled by varying the flow rate of cooling water, steam or refrigerant.

CHAPTER 3

PROCESS AND EQUIPMENT DESIGN



3.1. Feed Preparation

Propane is delivered to the plant in a pressurized liquid form, but is vapourized for use [22]. It is transported and delivered at ambient temperature. The minimal pressure at which propane is in liquid form at 25°C is 952.3 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 420 kPa and a temperature of -3.8°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 using high-pressure steam, which lowers the duty of the subsequent fired heater. A pressure drop of 10 kPa has been estimated for both units based on heuristics for boiling fluids in heat exchangers [2]. The final pressure of the feed stream, before entering the reactor, is 400 kPa.

3.2. Reaction System

3.2.1. Reactor

In industrial processes, the reactor employed consists of a set of stacked radial flow reactors where the catalyst flows down by gravity. The gaseous product is drawn between each stage and reheated in a fired heater, due to its endothermic nature, before being reintroduced in the following stage.

Harris *et al.* [19] has determined that the aromatization of propane over Ga-HZSM-5 (a Ga-doped HZSM-5) reaches an optimal aromatics selectivity at 520°C. The kinetic scheme presented by Corbetta *et al.* [9] was developed from kinetic data acquired over the 500-550°C temperature, based on the work of Nguyen *et al.* [23] and Bhan *et al.* [24]. A temperature in the 500-550°C range is expected to result in a good aromatics yield, although this will need to be confirmed through simulations. There is a compromise between the reaction rate, the selectivity of product and catalyst coking.

Process performance is highly dependent on the pressure in the reactors [25]. The maximum yield for the production of aromatics is achieved at low pressures because of the minimal hydrocracking occurring at this condition [7]. At high pressures, the proportion of heavy aromatics in the final product is higher [19]. On the other hand, a reaction performed at high

pressure uses only half of the catalyst needed compared to the low pressure process [25] because of the increased reaction rate [7]. The reaction kinetics were obtained at atmospheric pressure, and the final simulation of the reaction system should then be performed at this operating condition due to limited availability of kinetic data.

The model describing the evolution of the reaction in this type of reactor has been described in the literature [26], but is quite involved. Due to limitations with the simulation software, each reactor stack is modelled as a series of adiabatic packed bed reactors (PBRs) as done by Corbetta *et al.* [9] with interstage heating in a fired heater, as supported by heuristics and literature [7], [21].

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 [27]. 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 [28]. Solving the system accurately would require step sizes that are prohibitively small, making the methods impractical [29]. 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 [28]. Corbetta *et al.* report that implementation of such methods should be conducted using an external software (i.e. outside the simulator) [9]. This is in line with the observation that UniSim consistently fails to provide a passable solution to the systems of ODEs in the PBRs, possibly because its numerical methods cannot handle very stiff systems. The issue was reported to the UniSim technical staff who could not suggest an effective solution as of now, although they are currently discussing the possible causes of the issue.

Multiple possible remedies 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 where a somewhat realistic simulation is achieved.

Other possible solutions are currently being assessed and include the implementation of the Euler's backward method in Visual Basic (VBA), a time-consuming option, or the use of another process simulator such as AspenTech's Aspen Plus or the open-source DWSIM [30] which is claimed to implement numerical libraries for stiff ODE systems.

The current simulation does not implement a reactor. The reactor effluent composition for a single-pass of pure propane published by Harris *et al.* [19] for a specific set of conditions (520°C, 400 kPa) was simulated. This composition may not correlate with the reaction scheme reported by Corbetta *et al.* [9] which was developed for 500°C and 120 kPa. In absence of any other evident solutions, this was taken as a temporary initial estimate which is required to develop a preliminary separation strategy.

The absence of a reactor in the simulation flowsheet has severely limiting consequences. For instance, it is currently impossible to implement a realistic recycling strategy, as the reactor influent would contain reactive species other than propane, making the reactor effluent composition unpredictable. Furthermore, optimization of downstream separation operating conditions is futile, as the real properties (temperature, pressure and composition) of the reactor effluent with recycle cannot be predicted at this time.

3.2.2. Catalyst Regeneration

The stacked reactors of the Cyclar process host ZSM-5 catalyst [7]. A deposit of coke forms on the catalyst [25] at a rate lower than 0.02 wt% of the feed [7]. This low deposition rate insures mild regeneration requirements and a longer catalyst life [7]. 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 [7]. The regenerator is independent of the rest of the process and therefore can be run at independent conditions or be shut down momentarily without affecting the process [25]. The major factors influencing the needed amount of catalyst and the regeneration rate are the aforementioned reaction pressure [25] 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 [25]. This last factor supports the design choice of a feedstock of propane 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 to the catalyst regenerator and to the top of the reactor stack [21]. A detailed regeneration system is presented in Figure 10.

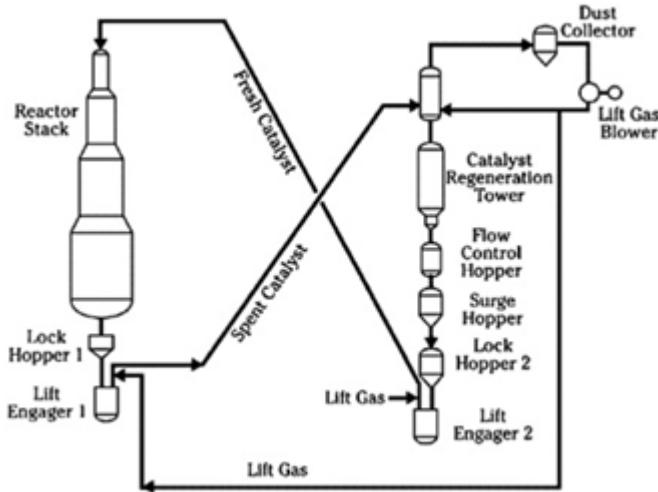


Figure 10 – Catalyst continuous regeneration system (adapted from [7])

The available UniSim fluid packages do not allow the simulation of catalyst regeneration. Since the CCR systems allows a complete regeneration of the catalyst [7], it was assumed, for simulation purposes, that the catalyst does not coke or deactivate and implementation of the unit in the simulation was disregarded.

3.3. 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. Most subsequent separations were done in distillation units as it is the second most economical method to separate compounds, and because separation was easily performed on the basis of difference in boiling points. An absorber was used to perform a separation of compounds with cryogenic boiling points to prevent the implantation of an expensive cryogenic separation process. The details of the design of the separation processes are presented in this section.

3.3.1. Flash Separation

The reactor effluent is cooled to 10°C before being sent to the flash vessel. This temperature was chosen because at higher temperatures, a high fraction of the toluene, benzene and xylenes were present in the vapour phase, which would lead to the product distributed between two streams. Furthermore, at temperatures around -40°C, the propane would condense and be present in the liquid phase, which would increase the amount of separations necessary for the liquid products. The first cooler utilizes cooling water, in order to cool the stream to a temperature of 45°C. This temperature was chosen with according to heuristics and a minimum approach temperature of 10°C. Therefore, cooling water available at 25°C would be heated to 35°C in order to cool down the reactor effluent. The initial cooling is performed to reduce the amount of refrigerant needed and duty of the subsequent cooling unit, to achieve the desired temperature of 10°C.

The reactor effluent is at a pressure of 380 kPa due to the pressure drop across the coolers downstream of the flash vessel. The stream is then flashed at atmospheric pressure to ensure that the light hydrocarbons and the hydrogen remain in the vapour phase.

3.3.2. Propane, Hydrogen and Fuel Gas Recovery

Since approximately 10% of the toluene is present in the vapour phase, an absorption column was added to recover as much toluene as possible. Simulation trials have shown that toluene, benzene as well as xylenes have an affinity to TEG since most of these compounds in the feed were present in the liquid stream. Furthermore, the lack of TEG in the vapour stream indicates that it is a good absorbent since it is non-volatile. Therefore, TEG is used as the absorbing agent. The TEG is fed into the column at 25°C and 101.3 kPa. These conditions are used because the TEG needs to be in liquid phase since it is the absorbent. The operating pressure of 101.3 kPa was chosen to avoid a pressure differential between the gas and liquid streams. The composition of the liquid and vapour stream at the exit of the absorption tower can be found in Table 16 of Appendix D – Simulation Summaries.

The liquid stream from the absorption tower is pressurized due to the large pressure drop observed in the heater downstream. It is then heated to 200°C prior to the distillation tower to boil off the BTX. The heated stream is then sent to the distillation tower to recover the TEG from the BTX-TEG mixture. The normal boiling point of TEG is 285°C and therefore, it is the heavy

key in this mixture. TEG with high purity is recovered as the condensate. The recovered TEG is cooled to 25°C and pressurized to 101.3 kPa to match the inlet conditions of the make up TEG stream. A portion of the recovered TEG is purged to prevent accumulation. The distillate from the column is sent to a train of distillation towers in order to separate the aromatic compounds.

The vapour stream from the absorption column is sent to a distillation tower. This distillation is to recover the propane as a heavy key. This separation is done to recover the high purity propane in order to recycle it to the process feed stream.

The distillate fraction contains hydrogen, methane and ethane, which will be burned to recover heat. This stream is not distilled due to the volatile nature of the compounds, which would lead to immense operating costs.

3.3.3. Benzene, Toluene and Xylenes Recovery

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 [25] since the final paraffin content is low [31]. The properties of benzene, xylenes and toluene allow the separation of these compounds based on their boiling temperatures [32].

3.3.3.1. BTX Separation Tower

The first distillation column (T-401) in the aromatics separation system is used mainly to recover propane and any traces of hydrogen, methane and ethane that have been entrained in the BTX mixture. The feed of the column consists of a mixture of the flash /vessel liquid outlet (V-201) and the vapour distillate from the TEG regeneration tower (T-303). The feed enters at conditions of 51°C and 101.3 kPa. These temperatures and pressures have been chosen based on the boiling point of the impurities and BTX. The distillate of the column contains 94.3 wt% of propane along with traces of hydrogen, methane and ethane. The stream exists at atmospheric pressure and -23.76°C, to ensure that the compounds are in the vapour phase. The bottoms consist of 26.9 wt% benzene, 24.6 wt% xylenes and 48.2 wt% toluene. The aromatics are at a temperature of 99.5°C, at atmospheric pressure and in the liquid phase. The mixture of BTX is then sent to the second distillation column. Propane is recycled and mixed with the propane feed to increase the overall conversion. A small portion of propane is purged to avoid accumulation in the system.

3.3.3.2. Benzene Distillation Tower

The purpose of this separation unit is to recover benzene at a high purity in order to sell it as a co-product. The liquid mixture of aromatics exiting T-401 enters the benzene distillation tower (T-402) at a temperature of 99.50°C, as the boiling point of benzene is 80.1°C at atmospheric pressure while the next more volatile component, toluene, vapourized at 110.6 °C. Benzene is recovered in the gas phase, as a distillate of 98.6 wt%, at a temperature of 80.54°C and atmospheric pressure. The bottoms, recovered in the liquid phase, consist of 33.6% xylenes and 65.4% toluene. This stream leaves the distillation tower at a temperature of 116.7°C and atmospheric pressure before entering the final distillation column, T-403.

3.3.3.3. Toluene Distillation Tower

The last distillation column, T-403, separates the last two aromatic compounds: toluene and xylene. The inlet feed is at 116.7°C and atmospheric pressure as, at these conditions, toluene goes in gas phase while xylenes are in liquid phase. Since toluene is more volatile and the main product, it is recovered as a distillate having a purity of 98.4%. This toluene is extracted at a temperature of 110.1°C and atmospheric pressure, to ensure it is in the vapour phase. Therefore, the bottoms consist of the liquid xylenes. This final stream exits at 139.9°C and atmospheric pressure.

3.4. 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 [2], [33]. 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 [2].

VLE are modeled with equations of state (EOS) or activity-coefficient models (ACM) [2]. 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 [2].

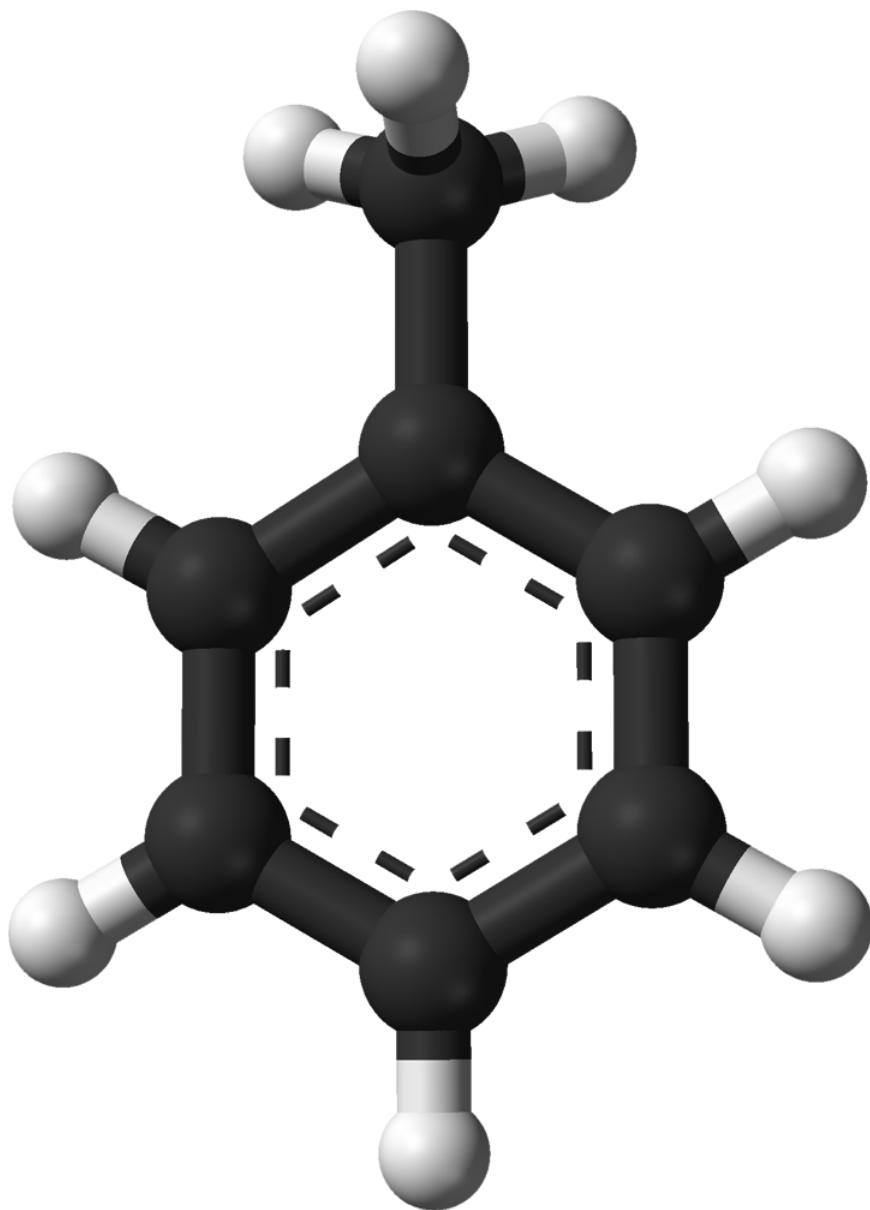
The aromatization of propane in the Cyclar process involves non-polar hydrocarbons exclusively, providing a rationale for the use of an EOS-based fluid package in unit operations where the species are in gas phase. Turton *et al.* [2] recommend using the Peng-Robinson (PR) or Soave-Redlich-Kwong (SRK) EOS. There is some evidence that both models produce similar results all else being equal [34], although the PR EOS models liquid systems significantly better in exchange of a poorer predictive ability for polar systems [35], [36].

Corbetta *et al.* selected the SRK EOS to simulate the Cyclar process [9], 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). In addition, since triethylene glycol (TEG) was used in the absorption column, the glycol fluid package was employed for that unit, in order to better predict the behaviour of the solvent.

CHAPTER 4

MISCELLANEOUS STUDIES



4.1. Optimization of Equipment

Given the current state of the simulation flowsheet, which lacks a reactor in working order, it is futile to attempt optimization of the downstream separation units, as the properties of the reactor effluent cannot be predicted accurately.

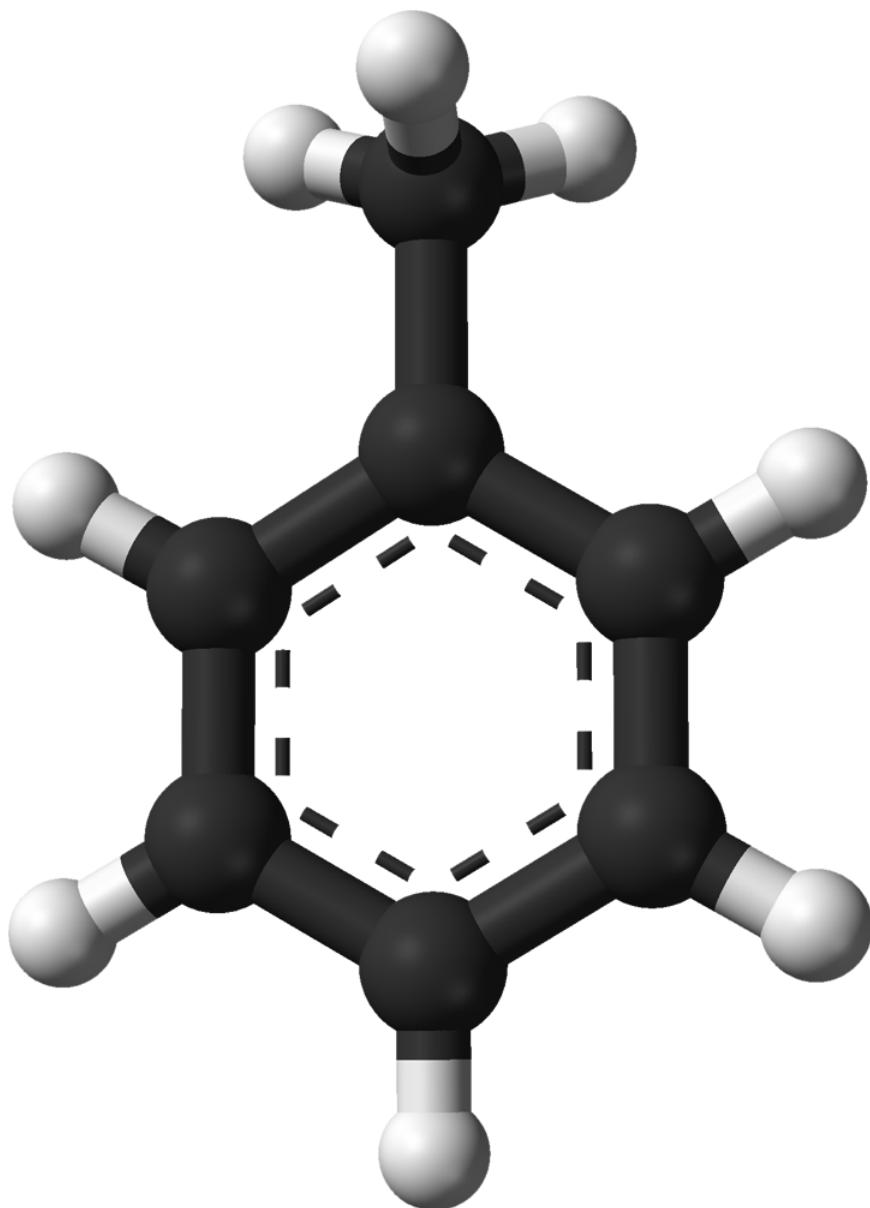
Even though useful case studies cannot be performed at this point, many case studies can be planned ahead such that they will be executed once a reactor can be properly simulated. Table 8 presents a list of case studies that will be performed

Table 8 – Preliminary list of case studies to be performed around the main process units

Unit Operation	Variable Controlled	Estimated Range of Study	Observed Response
Reactor (R-101)	Temperature	500 - 550°C	<ul style="list-style-type: none"> ● Selectivity ● Yield ● Apparent Conversion
Flash Vessel (V-201)	Pressure	101.3 - 303.9 kPa	<ul style="list-style-type: none"> ● Composition of liquid and vapour phases ● Composition of liquid and vapour phases
	Temperature	TBD	<ul style="list-style-type: none"> ● Recovery/purity ● Recovery/Purity ● Condenser duty ● Number of trays for at a constant recovery
Distillation Columns	Number of trays	Variable	<ul style="list-style-type: none"> ● Recovery/Purity ● Impact on type of utility required (cooling water vs. refrigerant) ● Duty ● Recovery/Purity
	Reflux ratio	1R _{min} - 2.5R _{min}	<ul style="list-style-type: none"> ● Condenser duty ● Number of trays for at a constant recovery ● Recovery/Purity ● Impact on type of utility required (cooling water vs. refrigerant) ● Duty ● Recovery/Purity
Absorption Unit (T-301)	Condenser and reboiler pressure	101.3 - 303.9 kPa	<ul style="list-style-type: none"> ● Recovery ● Solvent flow rate required for purity (cost)
	Condenser and reboiler temperature	TBD	<ul style="list-style-type: none"> ● Recovery ● Solvent flow rate required for purity (cost)
Absorption Unit (T-301)	Solvent	Various absorbing agents	<ul style="list-style-type: none"> ● Recovery ● Solvent flow rate required for purity (cost)
	Temperature	TBD	<ul style="list-style-type: none"> ● Column height
	Pressure	101.3 - 303.9 kPa	<ul style="list-style-type: none"> ● Column height

CHAPTER 5

OUTSIDE BATTERY LIMIT



5.1. Preliminary List of Utilities

Multiple utilities will be needed for adequate operation of the process: cooling water, high-pressure steam, medium pressure steam fuel gas and electricity. Major units concerned by each utility type are presented in Table 9.

Table 9 – Preliminary list of utilities

Utility	Units concerned
Cooling water	Heat exchangers: HX-201 HX-302
	Distillation columns condensers: T-302 T-303 T-401 T-402 T-403
Refrigerant	Heat exchangers: HX-202
High pressure steam	Heat exchangers: HX-101 HX-301
Medium pressure steam	Distillation columns reboilers: T-302 T-303 T-401 T-402 T-403
Fuel gas	Fired heaters: HX-102
	More fired heaters might be involved in the design of the reactor.
Electricity	Pumps: P-301 P-302

References

- [1] IHS, “Advances in Catalytic Reforming,” 2015. [Online]. Available: <https://www.ihs.com/products/chemical-technology-pep-advances-in-catalytic-reforming-2015.html>. [Accessed: 28-Jan-2016].
- [2] R. Turton, R. C. Bailie, W. B. Whiting, and J. A. Shaeiwitz, *Analysis, Synthesis, and Design of Chemical Processes*, 3rd ed. Boston, MA: Prentice Hall, 2009.
- [3] N. Weddle, “Europe naphtha, LPG cracker margins rise again on lower feedstock,” *ICIS*, 2015. [Online]. Available: <http://www.icis.com/resources/news/2015/05/11/9884322/europe-naphtha-lpg-cracker-margins-rise-again-on-lower-feedstock/>. [Accessed: 28-Jan-2016].
- [4] S. L. Peng, “Asia petchem plants could substitute 200,000 T of LPG for naphtha in June,” 2015. [Online]. Available: <http://af.reuters.com/article/commoditiesNews/idAFL4N0XX2NT20150507>. [Accessed: 28-Jan-2016].
- [5] S. L. Peng, “Demand, Asian petchem makers ditch LPG for naphtha after record 2014,” 2015. [Online]. Available: <http://www.fgenergy.com/corporate-media/fge-in-the-media/asian-petchem-makers-ditch-lpg-for-naphtha-after-record-2014-demand.aspx>. [Accessed: 28-Jan-2016].
- [6] ICIS, “Towards a New Aromatics Era,” 1994. [Online]. Available: <http://www.icis.com/resources/news/1994/01/04/35293/towards-a-new-aromatics-era/>. [Accessed: 28-Jan-2016].
- [7] L. Zhou, “BP-UOP Cyclar Process,” *Handbook of Petroleum Refining Processes*. 2004.
- [8] G. J. Antos and A. M. Aitani, *Catalytic Naptha Reforming*, 2nd ed. New York: Marcel Decker, 1995.
- [9] M. Corbetta, F. Manenti, C. Pirola, M. V. Tsodikov, and A. V. Chistyakov, “Aromatization of propane: Techno-economic analysis by multiscale ‘kinetics-to-process’ simulation,” *Comput. Chem. Eng.*, vol. 71, pp. 457–466, 2014.

- [10] G. E. Australia, “Saudi Aramco LPG Prices 2013,” 2013. [Online]. Available: <http://gasenergyaustralia.asn.au/reports-and-submissions/saudi-aramco-lpg-prices/saudi-aramco-lpg-prices-archives/saudi-aramco-lpg-prices-2013/>. [Accessed: 28-Jan-2016].
- [11] ICIS, “Rising US LPG production opens door for UOP aromatics tech,” 2013. [Online]. Available: <http://www.icis.com/resources/news/2013/04/22/9661448/rising-us-lpg-production-opens-door-for-uop-aromatics-tech/>. [Accessed: 28-Jan-2016].
- [12] Platt’s, “Methodology and Specifications Guide,” 2011. [Online]. Available: https://www.platts.com/IM.Platts.Content/methodologyreferences/methodologyspecs/asia_lpg.pdf. [Accessed: 28-Jan-2016].
- [13] “MSDS-Propane,” *Superior Propane*, 2014. [Online]. Available: https://www.superiorpropane.com/main/wp-content/uploads/2014/07/Propane_MSDS_ENG.pdf.
- [14] C. P. Association, “Understanding Propane Prices.” [Online]. Available: [http://www.propane.ca/sites/default/files/files/Understanding_Propane_Prices_E_2014\(1\).pdf](http://www.propane.ca/sites/default/files/files/Understanding_Propane_Prices_E_2014(1).pdf). [Accessed: 28-Jan-2016].
- [15] Index Mundi, “Propane Daily Price,” 2016. [Online]. Available: <http://www.indexmundi.com/commodities/?commodity=propane&months=360>. [Accessed: 28-Jan-2016].
- [16] Platt’s McGraw Hill Financial, “Platt’s Global Benzene Price Index,” 2016. [Online]. Available: <http://www.platts.com/news-feature/2014/petrochemicals/pgpi/benzene>. [Accessed: 28-Jan-2016].
- [17] P. M. H. Financial, “Platt’s Global Paraxylene (PX) Price Index,” 2016. [Online]. Available: <http://www.platts.com/news-feature/2014/petrochemicals/pgpi/paraxylene>. [Accessed: 28-Jan-2016].
- [18] J. A. Biscardi and E. Iglesia, “Structure and function of metal cations in light alkane reactions catalyzed by modified H-ZSM5,” *Catal. Today*, vol. 31, pp. 207–231, 1996.
- [19] J. L. Harris, N. Krisko, and X. M. Wang, “Aromatization of propane over a zeolite

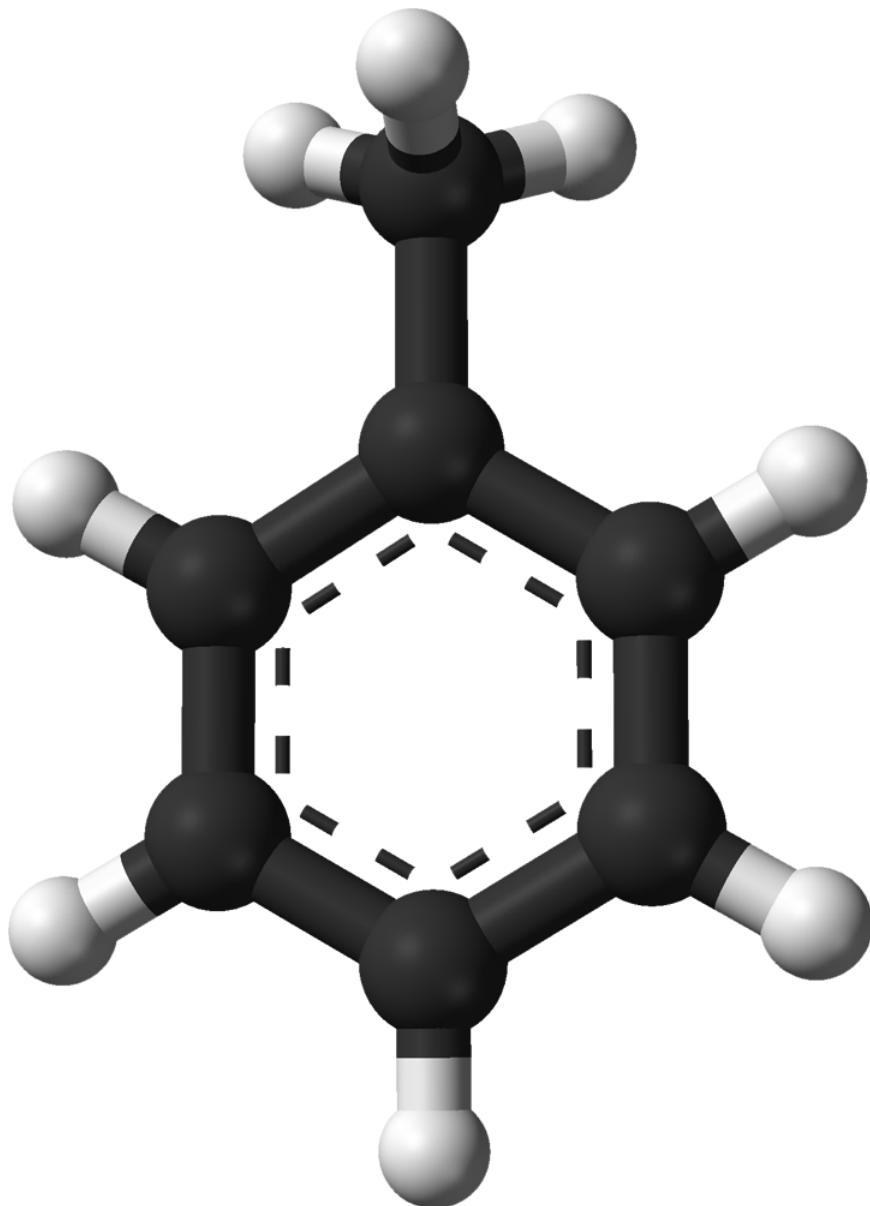
catalyst in both a microreactor and pilot plant,” *Appl. Catal. A Gen.*, vol. 83, pp. 59–74, 1992.

- [20] E. Dickson Ozokwelu, “Toluene,” *Kirk-Othmer Encyclopedia of Chemical Technology*. 2000.
- [21] S. M. Al-Zahrani, “Catalytic Conversion of LPG to High-Value Aromatics: The Current State of the Art and Future Predictions,” *Dev. Chem. Eng. Miner. Process.*, vol. 6, no. 1–2, pp. 101–120, 2008.
- [22] Canadian Propane Association, “About Propane.” [Online]. Available: <http://www.propane.ca/en/about-propane>. [Accessed: 11-Feb-2016].
- [23] L. H. Nguyen, T. Vazhnova, S. T. Kolaczkowski, and D. B. Lukyanov, “Combined experimental and kinetic modelling studies of the pathways of propane and n-butane aromatization over H-ZSM-5 catalyst,” *Chem. Eng. Sci.*, vol. 61, no. 17, pp. 5881–5894, Sep. 2006.
- [24] A. Bhan, S.-H. Hsu, G. Blau, J. M. Caruthers, V. Venkatasubramanian, and W. N. Delgass, “Microkinetic modeling of propane aromatization over HZSM-5,” *J. Catal.*, vol. 235, no. 1, pp. 35–51, Oct. 2005.
- [25] V. Zukauskas, “Aromatics,” *Encyclopedia of Hydrocarbons*, vol. II. Istituto Della Enciclopedia Italiana Fondata da Giovanni Treccani S.p.A., pp. 591–605, 2004.
- [26] R. G. Tailleur, “Cross-Flow Naphtha Reforming in Stacked-Bed Radial Reactors with Continuous Solid Circulation: Catalyst Deactivation and Solid Circulation between Reactors,” *Energy & Fuels*, vol. 26, no. 11, pp. 6938–6959, 2012.
- [27] S. Fogler, *Essentials of Chemical Reaction Engineering*, Intl. Ed. Boston: Pearson Education, Inc., 2011.
- [28] R. J. Kee, L. R. Petzold, M. D. Smooke, and J. F. Grcar, *Multiple Time Scales*. Orlando, FL: Academic Press, 1985.
- [29] S. C. Chapra and R. P. Canale, *Numerical Methods for Engineers*, 6th ed. New York, NY:

McGraw-Hill, 2010.

- [30] D. Medeiro, “DWSIM Wiki,” 2016. [Online]. Available: http://dwsim.inforside.com.br/wiki/index.php?title=Main_Page. [Accessed: 11-Feb-2016].
- [31] T. Foley, “CYCLAR™ Process Produces High-Quality Aromatic Products,” *Honeywell uop*, 2013. [Online]. Available: <http://www.uop.com/cyclar-process-produces-high-quality-aromatic-products/>. [Accessed: 28-Jan-2016].
- [32] W.-C. Chan and S.-P. Yang, “Adsorption of BTX compounds from aqueous solutions by water-insoluble starch,” *Die Angew. Makromol. Chemie*, vol. 251, no. 1, pp. 107–116, 1997.
- [33] D. Hill and F. C. Justice, “Understand thermodynamics to improve process simulations,” *Chem. Eng. Prog.*, vol. 107, no. 12, pp. 20–25, 2011.
- [34] C. H. Twu, J. E. Coon, and D. Bluck, “Comparison of the Peng–Robinson and Soave–Redlich–Kwong Equations of State Using a New Zero-Pressure-Based Mixing Rule for the Prediction of High-Pressure and High-Temperature Phase Equilibria,” *Ind. Eng. Chem. Res.*, vol. 37, no. 5, pp. 1580–1585, 1998.
- [35] S. Ramdharee, E. Muzenda, and M. Belaid, “A review of the equations of state and their applicability in phase equilibrium modeling,” in *International Conference on Chemical and Environmental Engineering*, 2013, pp. 84–87.
- [36] F. S. Manning and R. E. Thompson, *Oilfield Processing of Petroleum: Crude oil*. Tulsa, OK: Pennwell Books, 1995.

APPENDICES



Appendix G - Sample Calculations and Governing Equations

Thermodynamic Analysis

One of the factors used in the assessment of a chemical reaction pathway is the reaction spontaneity. This factor helps determine the speed and extent of a reaction. This analysis is done using the change in Gibbs free energy. The change in Gibbs free energy is defined as:

$$\Delta G = \Delta H - T\Delta S \quad \text{Equation G-1}$$

The change in Gibbs free energy is related to the equilibrium constant with Equation G-2:

$$\Delta G = -RT\ln(K_{eq}) \quad \text{Equation G-2}$$

For a chemical reaction, the standard change in Gibbs free energy can be found with Equation G-3:

$$\Delta G^\circ = \sum_i^{n \text{ product}} \gamma_i \Delta G_i^\circ - \sum_j^{n \text{ reactant}} \gamma_j \Delta G_j^\circ \quad \text{Equation G-3}$$

Where γ_x is the stoichiometric coefficient of chemical species X.

However, this only gives the change in Gibbs free energy at 25°C and 1 atm, and is not useful to calculate the energy at various temperatures. To surpass this limitation, the Van't Hoff equation can be used:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Equation G-4}$$

This equation assumes that ΔH° and ΔS° do not change in respect to temperature. ΔH° is found using the same equation for ΔG° , however it uses the enthalpy of formation.

The aromatization of propane is a complex reaction and a stoichiometric equation cannot be defined. Nonetheless it can be simplified to the following form [32]:



The plant is designed to produce toluene and therefore the chemical equation considered is:



The change of Gibbs free energy and enthalpy of toluene and propane in found in **Error! Reference source not found.**:

Table 10 – Thermodynamic properties of propane and toluene at standard conditions

Species	ΔH° [kJ]	ΔG° [kJ]
Propane	-105	24.3
Toluene	50.2	122

Using the thermodynamic data, the ΔG° and ΔH° can be calculated as follows:

$$\Delta G^\circ = (1 * 122 \text{ kJ}) - (1 * 24.3 \text{ kJ})$$

$$\Delta G^\circ = 97.7 \text{ kJ}$$

$$\Delta H^\circ = (1 * 50.2 \text{ kJ}) - (1 * -105 \text{ kJ})$$

$$\Delta H^\circ = 155.2 \text{ kJ}$$

The equilibrium constant at room temperature can be calculated with ΔG° and Equation G-2:

$$\Delta G^\circ = -RT \ln(K_{eq})$$

$$K_{eq} = e^{-\left(\frac{\Delta G^\circ}{RT}\right)}$$

$$K_{eq} = e^{-\left(\frac{97700}{8.3145*298}\right)}$$

$$K_{eq} = 7.32 \times 10^{-18}$$

The Van't Hoff equation can now be used to calculate the change of Gibbs free energy at any temperature, where K_1 is the equilibrium constant at 25°C. For example, at 850 K:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$K_2 = K_1 e^{\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$K_2 = 7.32 \times 10^{-18} * e^{\frac{155200}{8.3145} \left(\frac{1}{298} - \frac{1}{850}\right)}$$

$$K_2 = 3.40$$

The equilibrium constant can be used to find the change of Gibbs free energy at 850 K:

$$\Delta G^{850\text{ K}} = -8.3145 * 850 * \ln(3.40)$$

$$\Delta G^{850\text{ K}} = -8.65 \text{ kJ}$$

Mass Balance

The Cyclar process contains three main product streams: the aromatic, fuel gas and hydrogen streams. The overall mass balance can be given with Equation G-7:

$$\dot{m}_{in,propane} = \dot{m}_{out,propane} - \dot{m}_{Aromatics} - \dot{m}_{Hydrogen} - \dot{m}_{fuel\ gas} \quad \text{Equation G-7}$$

Table 11 represents the mass distribution of the products present in the Cyclar process.

Table 11 – Product mass distribution

Feedstock	Aromatic (wt%)	Fuel Gas (wt %)	Hydrogen (wt %)
100% Propane	63.1	31.0	5.9

The mass flow of each product can be calculated from the following equations:

$$\dot{m}_{out,propane} = (1 - x_{aromatics} - x_{fuel\ gas} - x_{hydrogen}) * \dot{m}_{in,propane} \quad \text{Equation G-8}$$

$$\dot{m}_{Aromatics} = x_{aromatics} \dot{m}_{in,propane} \quad \text{Equation G-9}$$

$$\dot{m}_{Fuel\ gas} = x_{fuel\ gas} \dot{m}_{in,propane} \quad \text{Equation G-10}$$

$$\dot{m}_{Hydrogen} = x_{hydrogen} \dot{m}_{in,propane} \quad \text{Equation G-11}$$

The aromatic fraction contains toluene, benzene, xylene and heavier aromatics (C_9+). The weight distribution is found in Table 12.

Table 12 – Weight distribution of aromatics

Compound	Mass fraction (%wt)
Toluene	41.1
Benzene	32.0
Xylene	18.8
Heavy aromatics (C_9+)	8.10

Therefore, the mass flow of each species can be found using the following equations:

$$\dot{m}_{Toluene} = x_{toluene} \dot{m}_{Aromatics} \quad \text{Equation G-12}$$

$$\dot{m}_{Benzene} = x_{Benzene} \dot{m}_{Aromatics} \quad \text{Equation G-13}$$

$$\dot{m}_{Xylene} = x_{Xylene} \dot{m}_{Aromatics} \quad \text{Equation G-14}$$

$$\dot{m}_{C9+} = x_{C9+} \dot{m}_{Aromatics} \quad \text{Equation G-15}$$

With a basis 120,000 MT/yr, the mass flow rate at the outlet of the process for all compounds can be evaluated, as follows.

$$\dot{m}_{out,propane} = (1 - 0.63 - 0.31 - 0.059) * 120000 \frac{MT}{yr} = 120 \frac{MT}{yr}$$

$$\dot{m}_{Aromatics} = 0.63 * 120000 \frac{MT}{yr} = 7.56 \times 10^4 \frac{MT}{yr}$$

$$\dot{m}_{Fuel\ gas} = 0.31 * 120000 \frac{MT}{yr} = 3.72 \times 10^4 \frac{MT}{yr}$$

$$\dot{m}_{Hydrogen} = 0.059 * 120000 \frac{MT}{yr} = 7.08 \times 10^3 \frac{MT}{yr}$$

The Cyclar process is used to produce toluene. Therefore, the mass flow rate of toluene needs to be evaluated.

$$\dot{m}_{Toluene} = 0.41 * 7.56 \times 10^4 \frac{MT}{yr} = 3.10 \times 10^4 \frac{MT}{yr}$$

$$\dot{m}_{Benzene} = 0.32 * 7.56 \times 10^4 \frac{MT}{yr} = 2.42 \times 10^4 \frac{MT}{yr}$$

$$\dot{m}_{Xylene} = 0.188 * 7.56 \times 10^4 \frac{MT}{yr} = 1.42 \times 10^4 \frac{MT}{yr}$$

$$\dot{m}_{C9+} = 0.081 * 7.56 \times 10^4 \frac{MT}{yr} = 6.12 \times 10^3 \frac{MT}{yr}$$

A summary of the overall mass balance is shown in Table 13:

Table 13 – Overall mass balance on the basis of 120,000 MT of propane per year

Compound	Mass input (MT/yr)	Mass output (MT/yr)
Propane	1.20x10 ⁵	120
Toluene	-	3.10x10 ⁴
Benzene	-	2.42x10 ⁴
Xylene	-	1.42x10 ⁴
Heavy Aromatics (C ₉ +)	-	6.12x10 ³
Fuel gas	-	3.72x10 ⁴
Hydrogen	-	7.08x10 ³

Preliminary Economic Analysis

Based on the mass flow rates of the chemical compounds used in the process, a simple economic analysis can be conducted with Equation G-16:

$$Profitability = \sum_i^{products} C_i * \dot{m}_i - \sum_j^{raw materials} C_j * \dot{m}_j \quad \text{Equation G-16}$$

Where C_x is the cost of component x in USD.MT⁻¹ and \dot{m}_x is mass flow rate of component x in MT/yr.

The cost of all components can be found in Table 14:

Table 14 – Costs of main components

Components	Cost of component (USD/MT)
Propane	345
Toluene	669
Benzene	740
Xylene	825
Hydrogen	1280

With the cost of every component from Table 14, the profitability of the process can be assessed:

$$\begin{aligned} \text{Profitability} &= ((669 * 3.10x10^4) + (740 * 2.42x10^4) + (825 * 1.42x10^4) \\ &\quad + (1280 * 7.08x10^3)) - (345 * 1.20x10^5) \frac{\text{USD}}{\text{year}} \\ \text{Profitability} &= 1.80x10^7 \frac{\text{USD}}{\text{year}} \end{aligned}$$

In conclusion, based on a simple economic analysis of the preliminary design for the Cyclar process, it is theoretically possible to profit 18 million USD a year.

Reaction Kinetics

The aromatization of LPG follows a complex set of chemical reactions. It was suggested by Harris *et al.* that the reaction could be kinetically modeled as a lumped first order irreversible reaction shown by Equation G-17.

$$(-r_P) = kC_P \quad \text{Equation G-17}$$

Where r_p is the rate of reaction in mol/time, k is the rate constant and C_p is the concentration of propane in mol/m.

Since the reaction is in the gas phase, the concentration of propane in respect to conversion may be calculated from Equation G-18:

$$C_p = C_{P0} \frac{(1 - X)}{(1 + \varepsilon X)} \quad \text{Equation G-18}$$

Where C_{P0} is the initial propane concentration, X is the conversion of propane and ε is the molar coefficient of expansion, which is calculated using Equation G-19 along with experimental data:

$$n = n_0(1 + \varepsilon X) \quad \text{Equation G-19}$$

Where n is the number of moles in the system and n_0 is the initial number of moles. Experimentally, it was determined that the molar coefficient of expansion was 1.1.

The reactor was modeled as a plug flow reactor. Equation G-20 represents the reactor's design equation.

$$W = F_{P0} \int_0^X \frac{dX}{(-r_p)} \quad \text{Equation G-20}$$

Where W is the mass of catalyst in kg, F_{P0} is the initial flow of propane in the system. Substituting the initial flow rate of propane as well as rate of reaction yields Equation G-21:

$$W = V_o C_{P0} \int_0^X \frac{(1 + \varepsilon X) dX}{k C_{P0} (1 - X)} \quad \text{Equation G-21}$$

Where V_o is the original volume. Equation G-21 can be integrated and rearranged to Equation G-22:

$$(1 + \varepsilon) \ln \left(\frac{1}{1 - X} \right) - \varepsilon X = k \frac{W}{V_o} \quad \text{Equation G-22}$$

Where W/V_o is defined as the catalyst contact parameter and is calculated with Equation G-23:

$$\frac{W}{V_o} = \frac{44}{WHSV} * C_{P0} \quad \text{Equation G-23}$$

Where WHSV is the space velocity in hr^{-1} . When the left side of Equation G-22 is graphed versus Equation G-23, a straight line passing through the origin is obtained with a slope of k . These k values can be fitted with the following Arrhenius expression of temperature:

$$k = A e^{-E_a/RT} \quad \text{Equation G-24}$$

Where E_a is the activation energy in J/mol and R is the universal gas constant (8.314 J/mol K). The experimental data from Harris *et al.* was used to plot the left side of Equation G-22 versus Equation G-23 and yielded Figure 11.

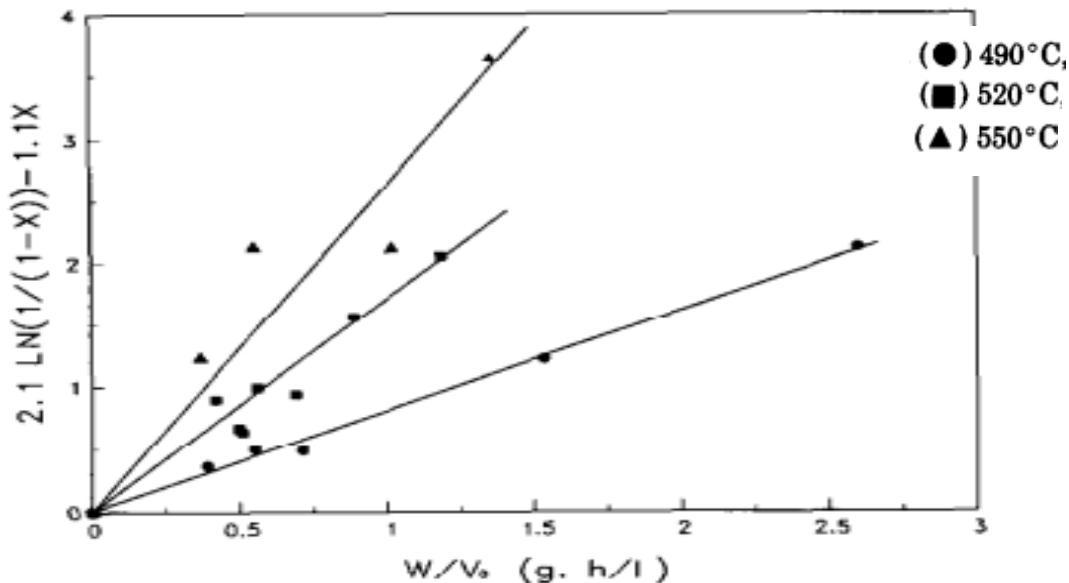


Figure 11 – Pilot plant conversion of propane as a first order irreversible reaction [32]

The data from Figure 11 was fitted to the Arrhenius relationship, obtaining a fitting coefficient of $R^2=99.8\%$. Using an activation energy of 86,850 J/mol, the following Arrhenius expression, representing the rate law as a function of temperature was obtained.

$$k = 8.679 \times 10^5 e^{-86850/RT} \quad \text{Equation G-25}$$

Appendix D – Simulation Summaries

Table 15 – Distillation tower specifications

Tower	Minimum Reflux Ratio	Number of Trays	Optimal Feed Tray	Product Purity (%wt)
T-302	0.107	12	7	99.17
T-303	0.116	4	2	99.98
T-401	0.198	4	3	94.32
T-402	1.95	19	11	98.68
T-403	1.19	37	14	98.36

Table 16 – Compositions of chemicals in the absorption tower

Compound	Inlet Mass Flow (kg/h)	Vapour Stream Mass Flow (kg/h)	Liquid Stream Mass Flow (kg/h)
Toluene	1.51	-	1.49
Benzene	2.66	0.75	1.91
Xylenes	0.20	-	0.2
Propane	53.5	53.4	-
Methane	10.1	10.1	-
Ethane	8.52	8.52	-
Hydrogen	2.19	2.19	-
TEG	99.4	-	99.3

Table 17 - Compositions of chemicals in the flash vessel

Compound	Inlet Mass Flow (kg/h)	Vapour Stream Mass Flow (kg/h)	Liquid Stream Mass Flow (kg/h)
Toluene	11.8	1.51	10.3
Benzene	7.34	2.66	4.68
Xylenes	6.01	0.20	5.81
Methane	10.1	10.1	-
Ethane	8.54	8.52	0.020
Propane	54.0	53.5	0.51
Hydrogen	2.19	2.19	-

Appendix J – Ethics Agreement and Task Allocation Sheet

Personal Ethics Agreement Concerning University Assignments

Group Assignment/Report

We submit this assignment and attest that we have applied all the appropriate rules of quotation and referencing in use at the University of Ottawa. We also confirm that we have taken knowledge of and respected the *Beware of Plagiarism!* brochure found at <http://www.uottawa.ca/plagiarism.pdf>. We attest that this work conforms to the rules on academic integrity of the University of Ottawa. We understand that this assignment will not be accepted or graded if it is submitted without the signatures of all group members.

ROXANNE GAUTHIER-FERLAND
Name, Capital letters

7032310
Student number

Roxanne gf
Signature

2016/02/12
Date

KARIM FRANÇOIS CHARIH
Name, Capital letters

6131125
Student number

KCF Charih
Signature

2016/02/12
Date

KATHERINE BOUCHARD
Name, Capital letters

6788979
Student number

Katherine Bouchard
Signature

2016/02/12
Date

ERIC TURRIFF
Name, Capital letters

6793776
Student number

Eric Turiff
Signature

2016/02/12
Date

Student Names:

- E.T. (Eric Turriff)
- K.B. (Katherine Bouchard)
- K.F.C. (Karim François Charih)
- R.G.F. (Roxanne Gauthier-Ferland)

Section	Lead Author	Co-Author(s)	Editing
<i>Executive Summary</i>	K.F.C.		All
<i>Chapter 2 – Process Description</i>			
2.1. Process selection	K.F.C.		All
2.2. Process Overview			
2.2.1. Raw Materials and Preliminary Cost Estimation	K.F.C.		All
2.2.2. By-Products and Co-Products	K.F.C.		All
2.2.3. Reaction Conditions and Kinetics			
2.2.3.1. Reaction Spontaneity	E.T.		All
2.2.3.2. Reaction Catalysis and Kinetics	E.T.		All
2.2.4. Block Flow Diagram	K.B.	R.G.F.	All
2.2.5. Overall Plant Material Balance	E.T.		All
2.3. Detailed Design Description			
2.3.1. Feed Preparation and Reaction System	R.G.F.		All
2.3.2. Preliminary Separation Process	R.G.F.		All
2.3.3. Light Hydrocarbons Recovery Process	R.G.F.		All
2.3.4. BTX Recovery Process	R.G.F.		All
2.4. Process Control Strategy			
2.4.1. Control in the Feed Preparation Section			All
2.4.2. Control in the Reaction Section	K.F.C.		All
2.4.3. Control of Downstream Separation Section	K.F.C.		All
	K.F.C.		
<i>Chapter 3 – Process and Equipment Design</i>			
Process Flow Diagram	K.B.		All
3.1. Feed Preparation	R.G.F.		All
3.2. Reaction System			
3.2.1. Reactor	K.F.C.		All
3.2.2. Catalyst Regeneration	R.G.F.		All
3.3. Separation Processes			
3.3.1. Flash Separation	E.T.		All
3.3.2. Propane, Hydrogen and Fuel Gas Recovery	E.T.		All

3.3.3. BTX Recovery	K.B.	All
3.3.3.1. BTX Separation Tower	K.B.	All
3.3.3.2. Benzene Distillation Tower	K.B.	All
3.3.3.3. Toluene Distillation Tower	K.B.	All
3.4. Thermodynamic Package Selection	K.F.C.	All

Chapter 4 – Miscellaneous Studies

4.1. Optimization of Equipment	K.F.C.	All
--------------------------------	--------	-----

Chapter 5 – Outside Battery Limit

5.1. Preliminary List of Utilities	R.G.F.	All
------------------------------------	--------	-----

Appendices

G. Sample Calculations and Governing Equations	E.T.	All
D. Simulation Summaries	E.T.	All
J. Task Allocation	K.B.	All

Other Tasks

Reference formatting	K.F.C.
Document formatting	K.B.
