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Thesis

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Optimization of the Operating Parameters of the Extractive Distillation Column (C-51) in the 200-Unit (RA1K) to Minimize Benzene Losses Using Aspen HYSYS.

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Abbreviations	Definitions
BTX	Benzene, Toluene, Xylene.
C51	Column 51
C55	Column 55
DCS	Distributed Control System.
ED	Extractive Distillation.
EDC	Extractive Distillation System.
FIC	Flow Indicator Controler.
GTC	Gas to Chemicals.
LIC	Level Indicator Controller
LLE	Liquid-Liquid Extraction.
MEA	Monoethanolamine.
ppm	Parts per million.
RA1K	Skikda refinery.
S/F	Solvent to Feed Ratio.
SRC	Solvent Recovery Column.
TDI	Toluene diisocyanate.
TNT	Trinitrotoluene.
UNIQUAC	Universal QUAsi-Chemical.
US EPA	United States Environmental Protection Agency.
US federal	United States federal.
USD	United State Dollars.
V.I	Viscosity Index.
WT %	percentage by weight.

Abstract
Benzene is a widely recognized and important aromatic hydrocarbon, highly valued in the chemical industry and on the international market, serving as a fundamental building block for numerous products. Various industrial processes and technologies have been developed to minimize benzene losses like GT-BTX process in unit-200 of Skikda refinery. Unit-200 underwent renovation as part of the rehabilitation of the refinery. This involved acquiring a license for a new GT-BTX process (extractive distillation) and modernizing the instrumentation, resulting in increased aromatic yield. However, after one year of unit operation, the quantity of recovered benzene is lower than the design specification. Our work will involve simulating and optimizing the Extractive Distillation Column 51 (C-51) using Aspen HYSYS V12.1, to minimize benzene losses and improve the separation efficiency. In order to accomplish that we have found that increasing the Solvent/feed ratio is the most impactful parameters to bring losses back within the design range.

Keywords
Benzene, Extractive Distillation, Simulation, Optimization, Column 51, Aspen HYSYS

Résumé
Le benzène est un hydrocarbure aromatique largement reconnu et important, très apprécié dans l'industrie chimique et sur le marché international, servant de base fondamentale pour de nombreux produits. Divers processus industriels et technologies ont été développés pour minimiser les pertes de benzène, tels que le procédé GT-BTX dans l'unité 200 de la raffinerie de Skikda. L'unité 200 a subi une rénovation dans le cadre de la réhabilitation de la raffinerie. Cela impliquait l'acquisition d'une licence pour un nouveau procédé GT-BTX (distillation extractive) et la modernisation des instruments, ce qui a entraîné une augmentation du rendement aromatique. Cependant, après un an de fonctionnement de l'unité, la quantité de benzène récupérée est inférieure aux spécifications de conception. Notre travail consistera à simuler et à optimiser la colonne de distillation extractive 51 (C-51) à l'aide d'Aspen HYSYS v12.1, afin de minimiser les pertes de benzène et d'améliorer l'efficacité de séparation. Pour y parvenir, nous avons constaté que l'augmentation du rapport solvant/charge est le paramètre le plus impactant pour ramener les pertes dans la plage de conception.

Mots clés
Benzène, Distillation Extractive, Simulation, Optimisation, Colonne 51, Aspen HYSYS

ملخص

البنزين هو مركب هيدروكربون عطري معترف به على نطاق واسع ومهم جدًا في صناعة الكيماويات وفي السوق العالمية، حيث يعتبر مكونًا أساسيًا للعديد من المنتجات. تم تطوير تقنيات صناعية متنوعة لتقليل خسائر البنزين مثل عملية GT-BTX في وحدة 200 في مصفاة سكيكدة. خضعت وحدة 200 لأعمال تجديد كجزء من تأهيل المصفاة، حيث تضمن ذلك الحصول على ترخيص لعملية GT-BTX جديدة (تقطير استخلاصي) وتحديث الأجهزة، مما أدى إلى زيادة العائد العطري. بعد سنة من تشغيل الوحدة، تبين أن كمية البنزين المستردة أقل من المواصفات التصميمية. ستشمل أعمالنا محاكاة وتحسين عمود التقطير الاستخلاصي 51 (C-51) باستخدام برنامج Aspen HYSYS v12.1، لتقليل خسائر البنزين وتحسين كفاءة الفصل. ولتحقيق ذلك، رفعنا نسبة المذيب إلى التغذية.

الكلمات المفتاحية
البنزين، تقطير استخلاصي، محاكاة، التحسين، عمود التقطير الاستخلاصي 51، Aspen HYSYS

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Finally, We would like to thank all those who have contributed, directly or indirectly, to the accomplishment of this work.

Dedication

I wholeheartedly dedicate this work to my beloved parents, whose immeasurable sacrifices, unwavering dedication, and tireless efforts have not only shaped the person I am today but have also filled my life with love, strength, and boundless inspiration.

I dedicate this work to my sisters, Sarah and Nassima, along with their beloved children Rym, Sirine, Anes, and Yahya. I also extend my heartfelt dedication to my right hand, my brother Mustafa Kamel. This work is a testament to the profound bond shared by our entire family, both near and distant relatives

I refrain from mentioning any specific friends to ensure that no one feels left out or upset by not being mentioned

I want to acknowledge the unwavering support of the 153, Bouira homies, my camping comrades, Sevda, the Boys, the MMA club, the friends from the village, Magra, and Babez. Without forgetting Ib for remaining true to himself. Your friendship and support have meant the world to me, and I deeply appreciate each one of you.

Mohamed Ali

Dedication

I dedicate this work to:

To my mother and my father.

To my brothers Abderrahim and Abdeldjalil.

To my sister Manar.

To my entire family.

To my partner Mohamed Ali.

To all my friends.

To all those who are dear to me.

Abdelmounaim

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General Introduction

BTX refers to benzene, toluene, and xylene, which are important aromatic hydrocarbons used in various industries. These compounds serve as feedstocks for plastics, solvents, fibers, and dyes. BTX compounds are derived from petroleum refining and are crucial for the development of efficient processes and maximizing economic value in different sectors

The petroleum industry employs methods like liquid-liquid extraction and extractive distillation to separate aromatics from lightweight reformate.

The process of extractive distillation plays an important role in the separation and purification of various chemical compounds. Extractive distillation columns are widely employed in the industry for separating azeotropic or close-boiling mixtures that cannot be efficiently separated by conventional solvent extraction techniques. Benzene, a highly valuable and widely used aromatic compound, is prone to losses during the extractive distillation process due to its close-boiling behaviour with other compounds present in the mixture.

Unit 200 of the Skikda refinery, where our studies were conducted, is designed to recover high-purity benzene and toluene from a feed called light reformate, which originates from a catalytic reforming unit.

Since its start-up, the unit has been utilizing liquid-liquid extraction as the aromatic separation process. However, due to its low efficiency and encountered challenges, Unit 200 underwent renovation in 2013 as part of the rehabilitation of the refinery. This involved acquiring a license for a new GT-BTX process (extractive distillation) and modernizing the instrumentation, resulting in increased aromatic yield.

However, after one year of unit operation, the quantity of recovered benzene is lower than the design specification.

Benzene is a lucrative product in the market. However, the loss of benzene has caused significant economic issues, resulting in a substantial decrease in supply.

The main objectives of this thesis are to simulate the extractive distillation column (C-51) in order to minimize the benzene losses in the 200 unit and meet the required design specifications.

By optimizing the operating parameters, it is possible to reduce the benzene losses, leading to improved process efficiency and cost-effectiveness

The simulation and optimization process will be carried out using Aspen HYSYS V12.1, a powerful process simulation software widely used in the industry for process design and optimization. Aspen HYSYS allows for accurate simulation of different columns and provides a platform to analyse the effect of various operating parameters on the separation performance.

In order to achieve our objectives, we took the time to organize the structure of our thesis. It has been divided into four chapters:

- The first chapter revolves around aromatics, providing a comprehensive discussion on BTX compounds and their distinct properties. We offer a general overview of BTX compounds, exploring their production methods and different separation techniques, including both conventional and intensified. Furthermore, we emphasize the economic status of BTX compounds, dedicating a section to their importance in various industries and applications;
- The second chapter contains a detailed description of the aromatic extraction unit (U-200) in Skikda Refinery, highlighting the important process variables;
- The third chapter explores the extractive distillation process, while conducting a comparison with the old process of liquid-liquid extraction to demonstrate the superiority and importance of extractive distillation;
- The fourth chapter represents the application and discussion section of this thesis, serving as the main part of our study. It is based on the monitoring of benzene losses and the simulation steps of column 51 for both the design and real cases, while conducting a comparison between them. The chapter also includes an analysis of the various operating parameters influencing C-51 with the aim of optimizing it by minimizing benzene losses.

We conclude our work with a general conclusion in which we summarize the main results of our study. Additionally, we provide recommendations for future research to offer clear, specific, and realistic suggestions for researchers who may conduct similar studies.

Chapter I

Introduction to Aromatics

Introduction

The rapid growth of aromatic hydrocarbons production, benzene, toluene, and xylene (BTX) of petroleum origin is due to the large market for these major intermediates and the existence of reforming and pyrolysis processes of gasoline, which make significant quantities of aromatic-rich cuts available.

I.1. Definition of Aromatics

Aromatics are unsaturated cyclic compounds composed of one or more benzene rings. The benzene ring has three double bonds with unique electron arrangements that make it quite stable Crude oils from various origins contain different types of aromatic compounds in different concentrations. Light petroleum fractions contain mono-aromatics such as toluene, xylene, and benzene. These compounds are important petrochemical feedstocks.

There are complex aromatic compounds consist of a number of ‘‘fused’’ benzene rings. These are known as polynuclear aromatic compounds. They are found in the heavy petroleum cut **[1].**

They are extensively studied due to their presence in various environmental settings and their high toxicity. In fact, this is one of the reasons that led to their inclusion in the list of priority pollutants by the United States Environmental Protection Agency (US EPA) **[2]**.

The number of hydrocarbons that can be encountered is limitless. Not only is there no limit to the number of fused rings, but the number of isomers increases significantly with the number of aromatic cycles. Furthermore, they can undergo alkylation. The most sought-after aromatic intermediates are benzene, toluene, and xylenes **[2]**.

BTX solvents are aromatic hydrocarbons that are used in a wide range of industrial applications to improve the product quality. BTX solvents are the major components of gasoline and are extensively used in the chemical processing operations **[2]**.

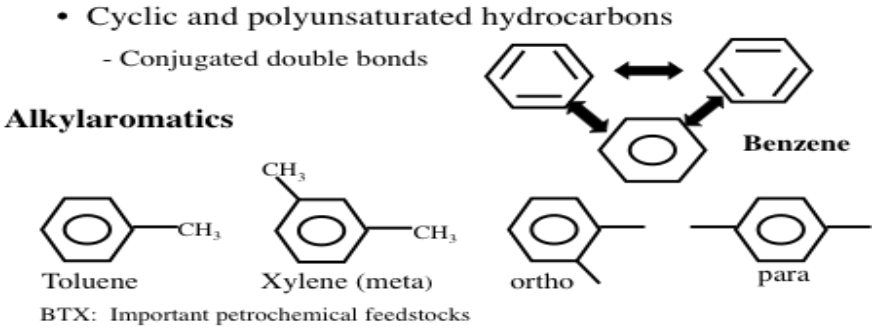


Figure I.1: *Simple aromatic compounds, benzene, toluene, xylene (BTX) and isomers of xylene.*

I.2. Benzene

Benzene has the formula C_6H_6, and all of the hydrogens are identical because substituting only one of the six hydrogens with a radical would yield only one compound. Therefore, the molecule must be symmetrical. The first formula for benzene proposed by Kekule is **[2]:**

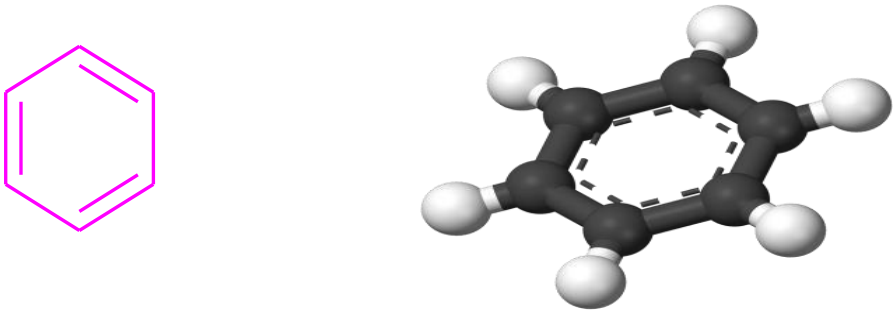


Figure I.2: *Benzene formula.*

I.2.1. Physical-Chemical Properties

At room temperature, benzene is a colourless liquid with a strong aromatic odour. It is less dense than water and practically insoluble in it (0.180 g per 100 g at 25 °C). Benzene is miscible with most organic solvents and forms azeotropic mixtures with water, certain alcohols, and hydrocarbons. It has a high refractive index, similar to that of glass. Its viscosity is lower than that of water **[1]**.

In infrared absorption spectroscopy, benzene exhibits an absorption band around 1500-1600 cm^ (-1) due to the vibrations of carbon-carbon bonds, and several absorption peaks between 650 and 1000 cm^ (-1) due to the vibrations of carbon-hydrogen bonds. The position and intensity of these peaks provide information about possible substitutions of hydrogen atoms **[2].**

The table below contains all the information regarding the physical and chemical properties of benzene:

Table I.1: *Physical-chemical properties of benzene* **[1].**

Property	Value
Molecular weight	78,11 g/mol
Melting temperature.	5,5 ºC
Boiling temperature.	80,1 ºC
Vapour pressure at 26.1 °C.	13,3 KPa
Density at 20 ºC	0,879 g/cm^3
Vapour density	2,70
Critical temperature	288,5 ºC
Critical pressure	4,83 MPa

I.2.2. Benzene Production

Benzene is produced when carbon-rich compounds undergo incomplete combustion. For example, it is naturally produced in volcanoes or forest fires. It is also present in cigarette smoke.

Until World War II, benzene was mainly a by-product of coke production in the steel industry. However, in the 1950s, the increasing demand for benzene, especially in the plastics industry, led to the need to produce benzene from petroleum. Currently, the majority of benzene is produced by the petrochemical industry, with a minor portion derived from coal **[1]**.

I.2.3. Utilisation of Benzene

Before the 1920s, benzene was commonly used as an industrial solvent, particularly for metal degreasing. When its toxicity became evident, it was replaced by other solvents for applications requiring direct user exposure.

Benzene is primarily used as an intermediate in the synthesis of other chemical compounds. The most widely produced benzene derivatives include styrene, used in the manufacturing of polymers and plastics, phenol, used in the production of resins and adhesives, and cyclohexane, used in the production of nylon.

Smaller amounts of benzene are used in the production of tires, lubricants, dyes, detergents, pharmaceuticals, explosives, and pesticides. In the 1980s, the main compounds produced from benzene were ethylbenzene (intermediate for styrene production) accounting for 48% of benzene consumption for synthesis, cumene 18%, cyclohexane 15%, and nitrobenzene 7%.

As an additive in gasoline, benzene increases the octane rating, thus acting as an antiknock agent. Therefore, until the 1950s, gasoline frequently contained a few percent of benzene until it was replaced by tetraethyl lead in the most commonly used antiknock additives. However, benzene has made a comeback in many countries due to its octane-boosting properties.

I.3. Toluene

Toluene, with the molecular formula C7H8, is a clear and colourless liquid at room temperature, emitting a strong and sweet odour similar to that of benzene. Its density is 0.8869 at 20°C. Toluene is slightly soluble in fresh water at 25°C **[2].**

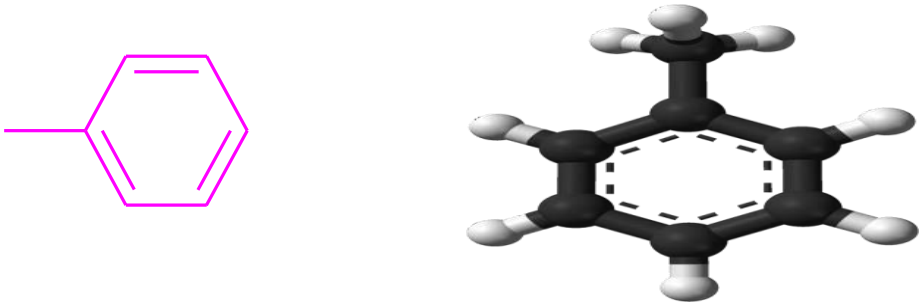


Figure I.3: *Toluene formula* **[2].**

I.3.1. Physical-Chemical Properties

At room temperature, toluene is a volatile, colourless liquid with an aromatic odor. Toluene is practically insoluble in water (0.535 g/L at 25 °C), but it is miscible with many organic solvents such as acetone, diethyl ether, chloroform, and ethanol. It is also soluble in glacial acetic acid **[1]**.

Table I.2: *Physical-chemical properties of toluene* **[1]**.

Properties	Value
Molecular weight	92,14 g/mol
Melting temperature.	9,3 °C
Boiling temperature.	110,6 °C
Vapour pressure at 26.1 °C.	3 KPa
Density at 20 °C	0,867 g/cm^3
Vapour density	3,14
Critical temperature	320 °C
Critical pressure	4 MPa

I.3.2. Toluene Production

Toluene is present in small amounts in crude oil. It is typically produced through catalytic reforming in the gasoline manufacturing process. It can also be obtained through cracking in the ethylene production process or from coal. The final purification of toluene is typically achieved through distillation or extraction methods **[1]**.

I.3.3. Utilisation of Toluene

Toluene is used to increase the octane rating in fuels. It also serves as a solvent in paints. It is used as a starting material for various industrial processes, including the synthesis of phenol, Trinitrotoluene (TNT), and toluene diisocyanate, which is necessary for producing polyurethane foam **[3]**.

I.4. Xylene

Xylene is a group of three isomeric aromatic hydrocarbon compounds: *ortho*-xylene (o-xylene), *meta*-xylene (m-xylene), and *para*-xylene (p-xylene). These compounds have the same molecular formula, C_8H_{10}, but differ in the arrangement of their carbon and hydrogen atoms within the benzene ring **[2]**.

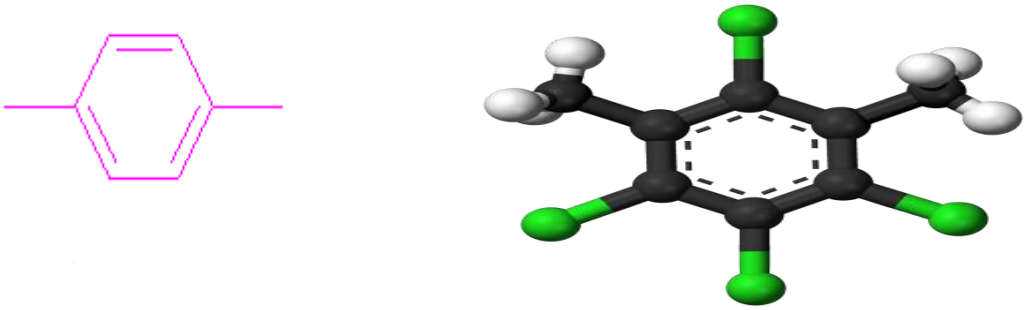


Figure I.4: *Xylene formula* **[2].**

Xylene contains three isomers **[2]**:

- Ortho-xylene;
- Meta-xylene;
- Para-xylene.

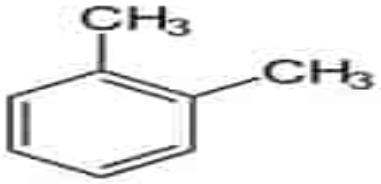


Figure I.5: *Ortho-Xylene formula.*

Figure I.6: *Meta-Xylene formula.*

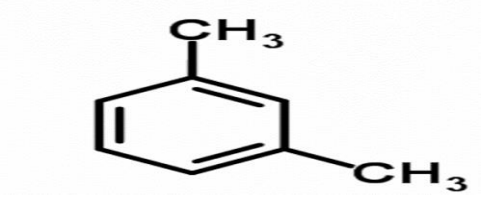


Figure I.7: *Para-Xylene formula.*

I.4.1. Physical-Chemical Properties

Xylene or dimethylbenzene is a group of aromatic hydrocarbons derived from methylated benzene. It is represented by three structural isomers: 1,2-dimethylbenzene, 1,3-dimethylbenzene, and 1,4-dimethylbenzene (commonly known as ortho-dimethylbenzene, meta-dimethylbenzene, and para-dimethylbenzene, respectively). Technical xylene is a mixture of the three isomers, with a composition approximately consisting of meta- (60%), ortho- (10-25%), and para- (10-25%) isomers **[1]**.

Xylenes are colourless liquids with a pleasant characteristic odour detectable at concentrations around 1 ppm. Xylenes are practically insoluble in water (0.02% by weight at 20°C) but are miscible with most organic solvents. Additionally, they are excellent solvents for fats, waxes, resins, etc **[1]**.

Under normal conditions of use, xylenes are stable products. They react with many compounds and are, in fact, important raw materials in organic synthesis **[1]**.

Table I.3: *The physical-chemical characteristics of xylenes* **[1]**.

	o-Xylene	**m-Xylene**	**P-Xylene**
Molecular weight	**106,16**	**106,16**	**106,16**
Melting temperature	**-25**	**-48°C**	**13 °C**
Boiling point	**144 °C**	**139 °C**	**138 °C**
Density	**0,8**	**0,86**	**0,86**
Vapour Pressure	**hPa at 20 °C**	**7.9 hPa at 20 °C**	**8.6 hPa at 20 °C**
Evaporation rate	**13,5**	**13.55 (diethyl ether = 1)**	**13.55 (diethyl ether = 1)**
Flash point	**27 to 32 °C (Closed cup)**	**25 à 27 °C (Closed cup)**	**25 to 27 °C (Closed cup)**
Autoignition temperature	**460°C**	**530 °C**	**530 °C**

I.4.2. Utilisation of Xylenes

- Para-xylene serves as the starting material for the production of the well-known synthetic textile known as Tergal or Terylene **[1]**;

- Ortho-xylene is used in the manufacturing of plasticizers, polyesters, and glyceryl phthalate-based paints **[1]**;
- Meta-xylene is also a raw material for the production of polyesters;
- Ethylbenzene can be dehydrogenated to produce styrene. The mixture of xylenes and ethylbenzene is used as a solvent **[3].**

I.5. Sources of Aromatics

Aromatics hydrocarbons are primarily obtained through catalytic reforming or steam cracking processes, which yield "aromatic gasoline." However, since the proportion of the latter does not meet the demand, additional transformations are necessary **[3].**

The distribution of various aromatic sources for chemical purposes in 2008 was as follows **[3]**:

- ✓ **72% comes from the reforming process:** This process is used by refiners to improve the octane rating of gasoline by producing aromatics. It generates a fraction rich in aromatic hydrocarbons called reformat, from which aromatics can be extracted and separated. The aromatic content of reformate varies depending on the composition of the feedstock, known as naphtha, as well as the severity of the reforming process. High-severity catalytic reforming is significantly preferred over low-severity catalytic reforming, which yields gasoline containing a higher amount of non-aromatic compounds.
- ✓ **24% comes from pyrolysis gasoline (steam cracking):** The primary role of pyrolysis gasoline is the production of short olefins such as ethylene and propylene. Typically, this process also produces a heavier fraction with a distillation range similar to gasoline, known as pyrolysis gasoline. This gasoline fraction is rich in benzene, toluene, and xylene (BTX), particularly benzene. Before its use, this fraction needs to undergo selective hydrogenation of diolefins to stabilize it.
- ✓ **4% comes from carbon:** Aromatics, especially benzene and toluene, can also have a non-petroleum origin and be derived from carbon. Catalytic hydrorefining (removal of sulphur, oxygen, and nitrogen compounds) of benzene obtained from the coal-to-coke transformation process yields a fraction rich in benzene and toluene, which can then be separated.

Table I.4: *Average mass compositions of aromatic gasoline obtained from high severity catalytic reforming and steam cracking* **[3].**

Aromatic	Reformate	Pyrolysis gasoline
Benzene	**25,6 %**	**41,5%**
Toluene	**23,1 %**	**19,1 %**
Ethyl Benzene (EB)	**4,6 %**	**7,9 %**
Paraxylene (pX)	**5,1 %**	**1,6 %**
Met xylene (mX)	**11,5 %**	**3,6 %**
Orth xylene (oX)	**6,6 %**	**2,1 %**
With aromatics	**17,4 %**	**17,6 %**
Non-Aromatic	**6,3 %**	**6,5 %**

In this table, we observe that the two main sources of aromatics have very different compositions, so depending on the market's needs, either one will be used. If the goal is to primarily produce benzene, pyrolysis gasoline is generally better suited; on the other hand, if xylene is desired, the use of reformate is significantly preferable **[3].**

I.6. Different Aromatics Separation Processes

Aromatics separation is a vital process in industries such as petrochemicals, pharmaceuticals, and fragrance/flavour production, where the separation of aromatic compounds plays a critical role. Aromatics, including benzene, toluene, and xylene, serve as key building blocks for a wide range of products, from plastics and polymers to medications and consumer goods. Conventional separation methods, such as distillation and extraction, have long been employed for aromatics separation **[4]**.

However, in recent years, intensified methods, including hybrid distillation systems **[5]**, reactive distillation **[6]**, membrane-based separation **[7]**, and adsorptive separation, have emerged as promising alternatives, offering enhanced efficiency, selectivity, and sustainability. These intensified methods integrate innovative technologies and processes to optimize the separation of

aromatics, enabling improved product quality, reduced energy consumption, and increased process efficiency **[8].**

I.6.1. Conventional Processes

Conventional methods of aromatics separation primarily include distillation, crystallization, adsorption, azeotropic distillation and extraction. These methods have been widely employed in industrial applications for the separation and purification of aromatics.

I.6.1.1. Distillation

Distillation is the most commonly used method for aromatics separation based on their boiling points. A mixture containing aromatics is heated, and the components with lower boiling points vaporize first and are collected. The vapour is then condensed to obtain the separated aromatic compounds. Distillation can be conducted in various types of distillation columns, such as packed columns or tray columns, depending on the specific requirements of the separation process **[4]**.

I.6.1.2. Crystallization

Aromatics separation using crystallization is a conventional method that exploits the differences in solubility and crystal formation properties of aromatic compounds **[9]**. The process involves cooling a solution or mixture containing aromatics to induce the formation of crystals, which can then be separated from the liquid phase **[10]**.

I.6.1.3. Adsorption

Adsorption processes exploit the affinity of aromatics for solid adsorbent materials. The mixture containing aromatics is passed through a bed or column packed with an adsorbent material. The aromatics preferentially adsorb onto the surface of the adsorbent, while the remaining components pass through. The adsorbed aromatics can then be desorbed using a suitable solvent or by changing the temperature or pressure, allowing for their separation **[4]**.

I.6.1.4. Azeotropic Distillation

Azeotropic distillation is a distillation process in which certain components can be added to the mixture to improve the separation process. Typically, water or benzene is added to the mixture as they can help increase the volatility of a substance. By the way, volatility refers to the ability of a substance to vaporize. In this process, the distillation can form an azeotrope, which can greatly aid in the precise separation process, as it will not alter the components as simple distillation would. Azeotropic distillation produces a heterogeneous mixture. In this process, an entrainer is used to trap particles in the stream in order to separate the azeotrope **[11]**.

I.6.1.5. Liquid-Liquid Extraction

Aromatic liquid-liquid extraction is a process that allows the separation of two or more components from a mixture by utilizing their uneven distribution between two practically immiscible liquids **[1]**.

Generally, an intimate contact is established between a feed solution containing the components to be separated (solute) and a second liquid phase called the solvent, which preferentially extracts one or more of the solutes. The solvent, now containing the solute, is referred to as the extract, while the feed solution, which has lost most of its constituent components, is called the raffinate **[1].**

I.6.2. Intensified Process

Intensified process of aromatics separation are innovative approaches that aim to enhance the efficiency, selectivity, and sustainability of the separation processes. Here are some examples of intensified process used for aromatics separation:

I.6.2.1. Reactive Distillation

Reactive distillation combines the separation and reaction processes in a single unit. By introducing a reactive component, such as an alcohol, during the distillation process, it becomes possible to selectively convert certain aromatic compounds into their corresponding esters. This simultaneous separation and reaction result in improved yields and reduced energy consumption compared to conventional distillation **[12]**.

I.6.2.2. Super Critical Fluid Extraction

Supercritical fluid extraction involves the use of supercritical fluids, typically carbon dioxide, as a solvent to selectively extract aromatics from the mixture. Supercritical fluids possess unique properties, combining the characteristics of both gases and liquids. This method offers high selectivity, avoids the use of hazardous solvents, and enables the recovery of aromatics under mild operating conditions **[12]**.

I.6.2.3. Membrane Separation

Membrane separation techniques, such as pervaporation and membrane pervaporation, utilise semi-permeable membranes to separate aromatics based on differences in molecular size and affinity. Membrane processes offer advantages such as low energy consumption, high selectivity, and the potential for continuous operation **[12]**.

I.6.2.4. Hybrid Separation Process

Hybrid separation processes integrate multiple separation techniques to achieve enhanced performance. For example, combining distillation with membrane separation or adsorption can enhance the overall separation efficiency, selectivity, and energy efficiency. These hybrid approaches leverage the strengths of different separation mechanisms to overcome limitations associated with individual processes **[13]**.

I.6.2.5. Extractive Distillation

Extractive distillation is a liquid-vapor process suitable for feed mixtures containing compounds from different chemical families with similar volatilities. This operation utilizes a solvent to achieve a chemical separation. The solvent creates or enhances differences in volatilities between the components to be separated. This method was traditionally used to produce a single component of high purity from a relatively narrow feed mixture that does not contain or contains very little aromatics (such as the extraction of benzene from a C6 cut). It has now been extended to the BTX extraction from a complete reformate **[1]**.

I.7. Importance of Aromatics in Petrochemical Field

The significant development of petrochemicals worldwide, linked to the growth of industries producing plastics, synthetic fibres, synthetic rubber, detergents, and numerous other organic chemical products, requires increasing quantities of hydrocarbon raw materials each year.

Given that the feedstock for petrochemical complexes primarily comes from petroleum and natural gas, the increasing demand for high-grade petrochemical raw materials, including olefins and aromatics, is on the rise **[14].**

For the latter, it is primarily benzene and paraxylene that show a growing demand.

Toluene is present in various petroleum fuels and is used as an extraction solvent in the cosmetic industry (perfumes) and the pharmaceutical-chemical industry. It is also used as a solvent or component in the production of paints, varnishes, lacquers, waxes, and inks (printing). Toluene serves as a starting material for various industrial processes, including the synthesis of rubber, phenol, TNT, toluene diisocyanate (TDI) used to produce polyurethane foam, benzene, xylenes, nitrotoluene, benzyl chloride, benzaldehyde, p-toluenesulfonic acid, vinyl toluene, etc. It is also

employed in the manufacturing of adhesives and glues, leather tanning, and as a booster for the coatings of certain table tennis players (despite its prohibition) **[15].**

Benzene is used as a solvent, particularly as a cerumenolytic agent. It is also employed by the printing, rubber, and leather industries. Benzene serves as a starting reagent for the production of terephthalic acid, which is used as a monomer for the production of terephthalate-type polymers.

Xylene is also used for cleaning purposes and as a pesticide. It is also utilized in parasitology. Xylene serves as a paint thinner and is found in paints and varnishes. It is present in small quantities in aviation fuels and gasoline. In the presence of oxidizing agents such as potassium permanganate ($KMnO_4$), the methyl group in xylene can be oxidized to form a carboxylic acid.

When both methyl groups are oxidized, o-xylene forms phthalic acid, while p-xylene forms terephthalic acid **[16].**

Ethylbenzene is primarily used in the petrochemical industry as a synthetic intermediate in the production of styrene, which is used to manufacture polystyrene. Styrene is obtained through catalytic dehydrogenation. Ethylbenzene is also employed as a solvent in paints and serves as an anti-knock additive in gasoline for automobiles **[17].**

I.8. Market Analysis and Insights of BTX Market

Data Bridge Market Research analyses that the BTX solvents market will witness a Compound Annual Growth Rate of 3.50% for the forecast period of 2022-2029. Growth in BTX solvents especially in the developing economies such as India and China, surging application of BTX solvents across various industries such as chemical processing, dye and others increasing investment by the government for research and development activities and surge in industrialization especially in the developing countries are the major factors attributable to the growth of the BTX solvents market. Therefore, the BTX solvents market value, which was USD 2,500 million in 2020, would rocket up to USD 3,407.24 million by 2029 **[18].**

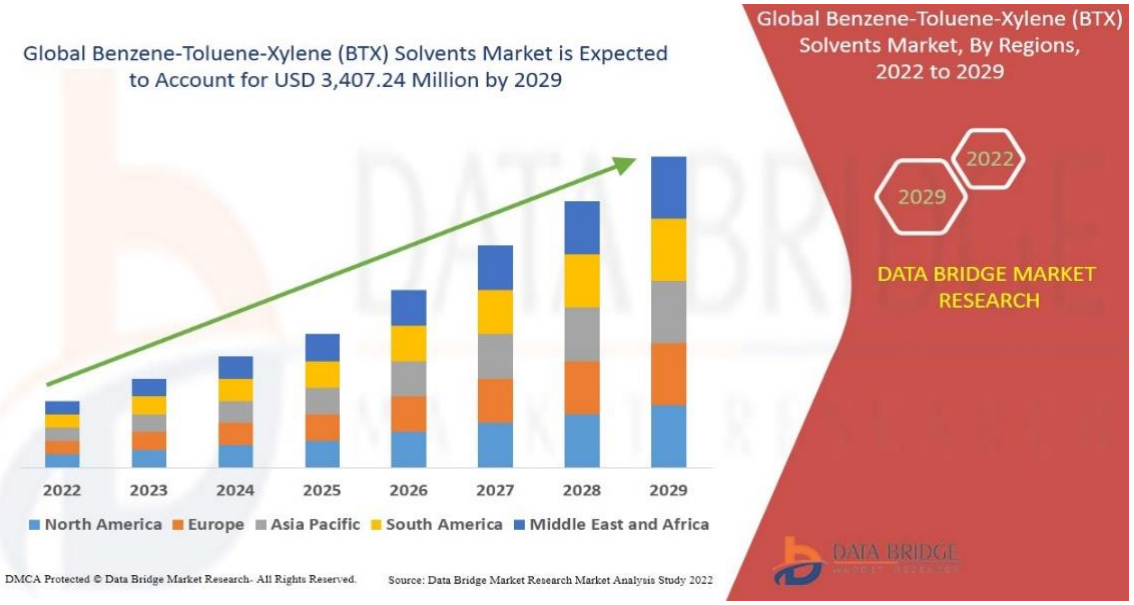


Figure I.7: *BTX market analysis by region 2022 to 2029* **[18].**

Conclusion

A significant portion of aromatics, especially benzene, toluene, and xylene (BTX), is derived from petroleum or crude oil. During the refining process.

aromatics are a diverse and fascinating group of compounds that play a significant role in various aspects of our lives. Their unique molecular structures and characteristic smells have made them valuable in industries such as perfumery, petrochemicals, pharmaceuticals, even food and beverage.

Aromatics play a crucial role in driving the economic development of the country. It is essential to implement aromatic production units in modern refineries with significant processing capacities to meet the specifications of the local and international markets.

Chapter II

Description of Unit-200

Introduction

GT-BTX^{SM} Extractive Distillation Technology for aromatics extraction has been successfully commercialized having several advantages over competing processes, in the areas most meaningful to the design and operation. GTC's technology features proprietary formulation of commercially available solvent that exhibits high selectivity and capacity, much improved operation, and less process equipment. This results in lower capital investment, lower energy consumption and lower operating cost **[19].**

This technology has been chosen by Societe Nationale de Raffinage de Petrole, Sontarach to revamp the existing Aromatic Unit-200 at Skikda Refinery, Algeria as part of the Aromatics Plant Rehabilitation Project, replacing the existing liquid–liquid extraction section with a new Extractive Distillation Unit by utilizing GT-BTX technology. A customized application of GT-BTX^{SM} extractive distillation technology has been provided to increase the unit capacity for high purity Benzene and Toluene production **[19].**

The Aromatics Plant Rehabilitation Project consists of revamping a series of existing units with the main scope of increasing the benzene and paraxylene production. The objective has been achieved by revamping existing units (Magnaforming, Aromatics Extraction and Paraxylene Unit) and by including a new process unit (Isomerization unit) to convert almost all the xylenes into paraxylenes **[19].**

The Aromatics Extraction Unit-200 in the revamp configuration processes the benzene-rich fraction from the Magnaformer Post-fractionation system, the benzene-rich fraction from the Platformate Splitter, and the benzene-toluene fraction from the Post-fractionation section of the Isomerization Unit **[19].**

The Aromatics Extractive Distillation Unit is designed for 4 feed cases **[19]**:

- RA1K Crude SOR – Isomerization SOR (RSIS Case)
- RA1K Crude EOR – Isomerization SOR (REIS Case)
- HBNS Crude SOR – Isomerization SOR (HSIS Case)
- HBNS Crude EOR – Isomerization EOR (HEIS Case).

II.1. The Role of Installation

Existing Unit–200 has been revamped in order to be able to process the combined aromatic-rich feeds, by converting the existing liquid-liquid extraction system to an extractive distillation

technology using GTC's GT-BTX process. The revamped unit allows higher aromatics recovery yields, higher benzene product purity and improved energy efficiency **[19].**

The post-fractionation section processes the aromatics extract obtained from the extractive distillation section. In all the cases the unit produces high-purity benzene and toluene products available at the battery limit for sale. In addition, the Aromatics Recovery Unit produces as auxiliary products a raffinate non-aromatic product with less than 1% aromatic content and a Toluene concentrate product with more than 99.9% toluene **[19].**

II.2. Extractive Distillation

The working principle of ED is the alteration of the relative volatility of components in the presence of a highly selective solvent. In a mixture containing aromatics and non-aromatics, the relative volatility of the non-aromatic components is enhanced over that of aromatic components in the presence of a solvent. This enhancement allows the non-aromatics to be distilled overhead in a conventional distillation column, while the aromatics are recovered in the column bottoms. The solvent used in the GT-BTX process is the proprietary blend, Techtiv-100SM, which makes it possible to achieve excellent process performance **[19].**

The general schematic flow diagram of the GT-BTXSM process is shown below and consists of two major towers: an extractive distillation column (EDC) and a solvent recovery column (SRC).

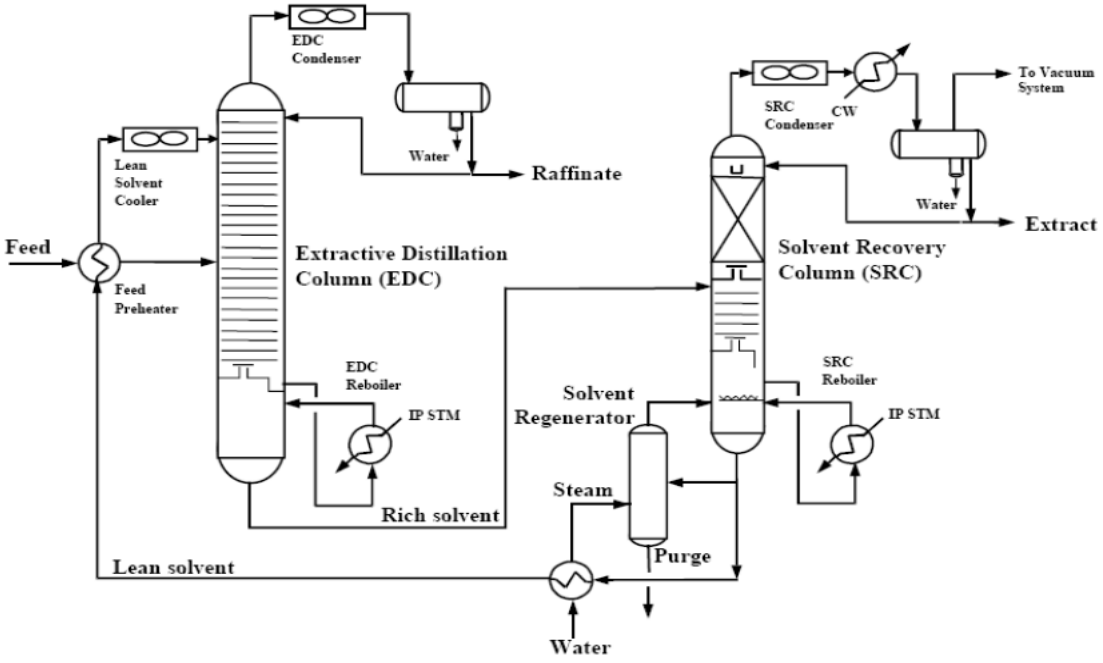


Figure II.1: *Process flow for GT-BTX^{SM} process* **[19].**

Hydrocarbon feed is preheated with hot circulating solvent and fed at mid-point into the EDC. Lean solvent is fed at an upper point and selectively extracts the aromatics into the tower bottoms, in a vapour/liquid distillation operation. The non-aromatic hydrocarbons exit the top of the column and pass through a condenser. A portion of the overhead stream is returned to the top of the column as reflux. This washes back any entrained solvent **[19].**

Rich solvent from the bottom of the EDC is routed to the SRC, where the aromatics are stripped overhead. Stripping steam is used to facilitate the stripping of the hydrocarbons. The SRC is operated under vacuum to reduce the boiling point at the base of the column. Lean solvent from the bottom of the SRC is passed through a series of heat exchangers, for heat recovery, before returning to the EDC. Aromatics overhead product from the SRC is condensed and withdrawn as extract and sent to the B/T Post-fractionation section for further processing by distillation, in order to produce final products, high purity benzene and toluene **[19].**

Water from the overhead of the EDC and SRC is collected and vaporized with hot solvent, and used as stripping medium. A solvent regenerator is used to continuously process a small portion of the circulating lean solvent. The regenerator distills the solvent away from heavy decomposition products, which are purged on a periodic basis from the regenerator bottoms.

Since the basic separation in the GT-BTX process is achieved by distillation, the operation of the unit is very simple and intuitive. Control of the main process parameters can be achieved in a manner very similar to that for a regular distillation column **[19].**

II.3. Process Description

The process description is based on the Process Flow Diagram, Piping and Instrumentation Diagrams. GTC's Overall process configuration involves the following sections **[19]**:

- **Extractive Distillation Section Including:**
  - Extractive Distillation;
  - Solvent Recovery;
  - Solvent Regeneration;
  - Steam generation and water circuit.

- **Post Fractionation Section Including:**
  - Clay Treatment;
  - Benzene Fractionation;
  - Toluene Fractionation.
- **Solvent storage system**
- **Extract Storage: Clay Charge Tank**

II.3.1. Extractive Distillation Section

II.3.1.1. Extractive Distillation Column

The operating conditions for the EDC, extractive distillation column 200-C-51, are as follows **[19]**:

- Top temperature: 86°C - 89°C
- Bottom temperature: 165 °C - 166 °C
- Top pressure: 0.67 Kg/cm^2 (g)
- Bottom pressure: 1.27 Kg/cm^2 (g)

II.3.1.2. Solvent Recovery Column

Solvent recovery is performed in the solvent recovery column, 200-C-55 The rich solvent containing solvent and aromatics introduced from the Extractive Distillation Column (EDC) 200-C-51 is fed at the Solvent Recovery Column (SRC) 200-C-55, below the packed section of the tower, on tray no.3. The specially designed feed distributor at feed entry is provided to handle very high amount of vapor generated due to flashing of the feed. Two de-entrainment trays are installed above the flashing feed to recover eventual solvent entrained to the top of the column. The column is provided with another 13 trays installed below the feed and one packing bed on the top section, installed above the two de-entrainment trays. The 13 trays below the feed are designed to handle high liquid solvent traffic moving down into the column. The packed section ensures that the volatile aromatics are completely separated from solvent. Lean solvent is recovered at the bottom of the column and is recycled to the extractive distillation column, 200-C-51, while the aromatics are stripped overhead **[19].**

In the SRC, aromatic hydrocarbons will be separated from the solvent producing a lean solvent quality at the bottom of the column, required for the extractive distillation operation. The column will operate under vacuum conditions to minimize the boiling point at the bottom of the column.

Furthermore, stripping steam originating from the water circuit will be injected at the bottom of the column to assist in the stripping of the aromatics **[19].**

The operating conditions for the solvent recovery column 200-C-55, are as follows **[19]:**

- Top temperature: 63 °C - 64 °C
- Bottom temperature: 175 °C
- Top pressure: -0.38 Kg/cm^2 (g)
- Bottom pressure: -0.21 Kg/cm^2 (g).

A small part of the lean solvent from the bottom of the SRC column (200-C-55) is directed at a controlled flow rate (200-FIC-1804) to the solvent regenerator, 200-C-52. Lean solvent from the SRC bottom 200-C-55 is pumped by SRC bottoms pump 200-MP-53A/B, through a series of heat exchangers to recover heat, and then routed back to the extractive distillation column. First, the lean solvent is used as heating source to vaporize process water in the steam generator 200-E-66. Next, it is used as heat medium for the feed preheater 200-E-51, for the water preheater 200-E-15, and for the extract preheater 200-E-52. Finally, the lean solvent is cooled in the lean solvent cooler 200-EA-1 up to the required temperature and sent to the EDC column (200-C-51). A small part of the lean solvent from the bottom of the SRC column is directed at a controlled flow rate to the solvent regenerator, 200- C-52 **[19].**

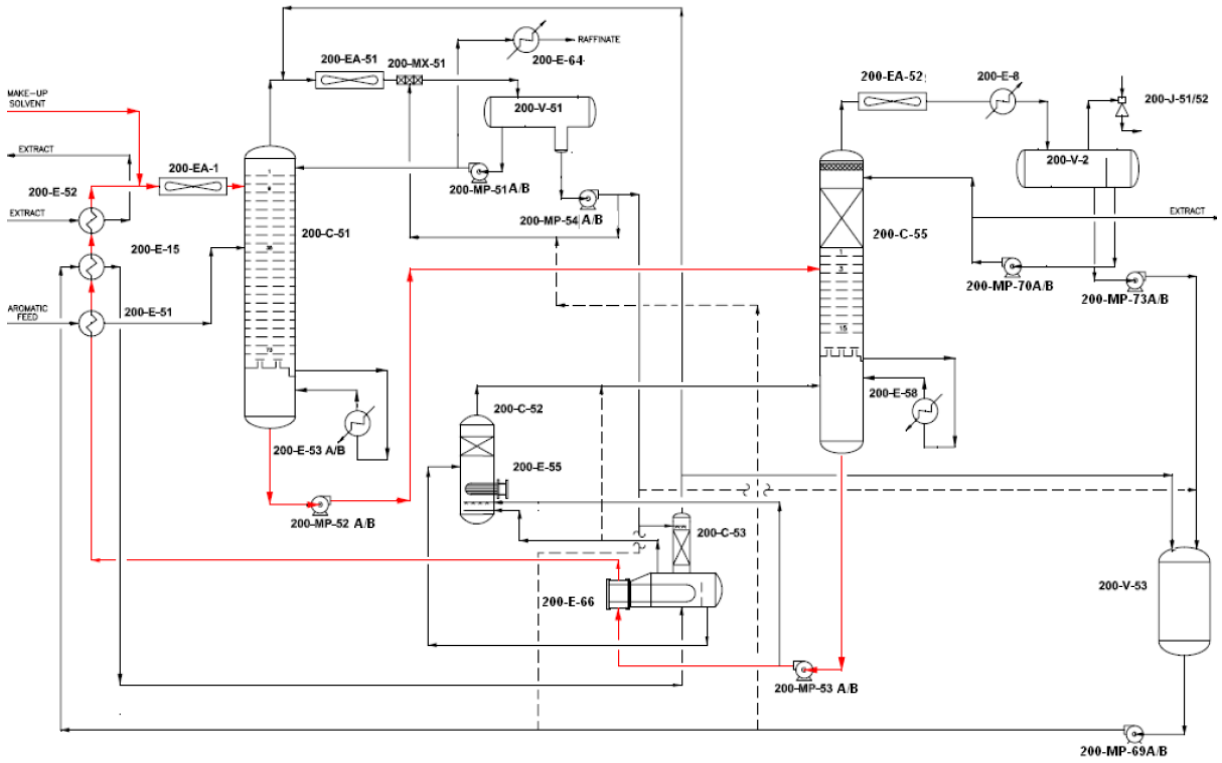


Figure II.2: *Solvent Recirculation* **[19].**

II.3.1.3. Solvent Regeneration

The solvent is stable under normal operation conditions. However, over a period of time, the solvent may slowly degrade at elevated temperature with air leak to the process. The degradation products are acidic in nature; therefore, requiring means to neutralize these acids to minimize any chance of corrosion in the unit. Monoethanolamine (MEA) shall be added to both the lean solvent and the process water at the inlet solvent line to the lean solvent cooler (200-EA-1), and to the EDC overhead receiver (200-V-51) water boot line, to adjust the pH of the solvent and / or water as necessary **[19].**

Heavy degradation products are removed from the system at the solvent regeneration system. A controlled portion of the lean circulating solvent is vaporized in the solvent regenerator 200-C-52. Stripping steam generated in the steam generator 200-E-66 is sent to the solvent regenerator (200-C-52) in order to assist in the vaporization of the solvent. In addition, a stab-in reboiler 200-E-55 is provided in the vessel to supply additional heat for regeneration. The heat input to the reboiler is regulated by controlling the IP Steam flow rate (200-FIC-1801), in cascade with the level control on the solvent regenerator (200-LIC-1801). The temperature of the solvent regenerator is not controlled and is automatically established by the steam/solvent ratio and flash point at the

operating pressure (vacuum). Because of this the solvent flow-rate to the solvent regenerator (200-FIC-1804) and the steam to the solvent regenerator (200-FIC-1802), need to be as much as possible constant. A solvent regenerator temperature at the level of 1750C is desired to be maintained **[19].**

The overhead vapor product of 200-C-52 consisting of steam and all vaporized solvent is sent to the SRC solvent recovery column, as stripping medium. The solvent regenerator is directly connected to the SRC bottom and because of this operates at the same SRC bottom pressure. The process piping between these vessels is as short as possible with smooth transitions for ease of flow and good heat transfer. Any heavy, degradation components will accumulate in the solvent regenerator sump and are purged manually on a periodic basis through a small heated knock out pipe into a small jacketed drum **[19].**

II.3.1.4. Steam Generation and Water Circuit

Heat recovery from the hot lean solvent as is mentioned above, is accomplished in a series of heat exchangers, one of these being the steam generator 200-E-66 where is generated steam from process water using as heat medium lean solvent **[19].**

Process water from various locations in the unit is collected and recovered. The amount of fresh process water addition is considerably less than required in a liquid–liquid extraction unit where the wash water step involves a substantial water inventory. The water loop in the extractive distillation process is typically closed, but if the hydrocarbon feed contains appreciable water, or an internal utility leak develops, water level can increase exceeding the process usage. Any excess water can be purged from one or more locations in the unit once the hydrocarbon / solvent impurity concerns have been addressed. The function of the water stripper, solvent regenerator, and steam generator are to handle the various process waters under normal conditions **[19].**

The process water from the SRC overhead receiver (200-V-2) accumulated in the water surge drum 200-V-53 is pumped by 200-MP-69A/B water surge pump, first to the water preheater 200-E-15 to preheat the process water up to 950C against the hot lean solvent and next to the steam generator 200-E-66 **[19].**

This kettle exchanger will vaporize the preheated process water producing stripping steam by using hot lean solvent as heating medium. The stripping steam generated in 200-E-66 is used to assist the stripping process in the SRC column and the vaporization of solvent in the solvent regenerator. The steam generated in 200-E-66 is sent at controlled flow rate (200-FIC-1802) to the

solvent regenerator 200-C-52. The amount of steam generated is controlled by the steam pressure control (200-PIC-1804) on the outlet line to the SRC column **[19].**

The water from the EDC receiver (200-V-51) water boot is pumped by the EDC water pump 200-MP-54A/B to the water stripper 200-C-53, where any trace amount of hydrocarbon contained in the water phase is stripped. A small portion of the steam produced in the steam generator 200-E-66 supplies the heat necessary for the non-aromatics removal in 200-C-53, water stripper. The stripper overhead vapor including stripped non-aromatics hydrocarbons is routed to the EDC condenser 200- EA-51 and the hydrocarbons from the water stripper overhead are removed to the raffinate product. Water level in the steam generator 200-E-66 is controlled by a signal selector (200-FY-1901) either by purging more or less water to 200-C-52 Solvent regenerator, or by controlling the water sent by 200-MP-69A/B to Steam generator 200-E-66 **[19].**

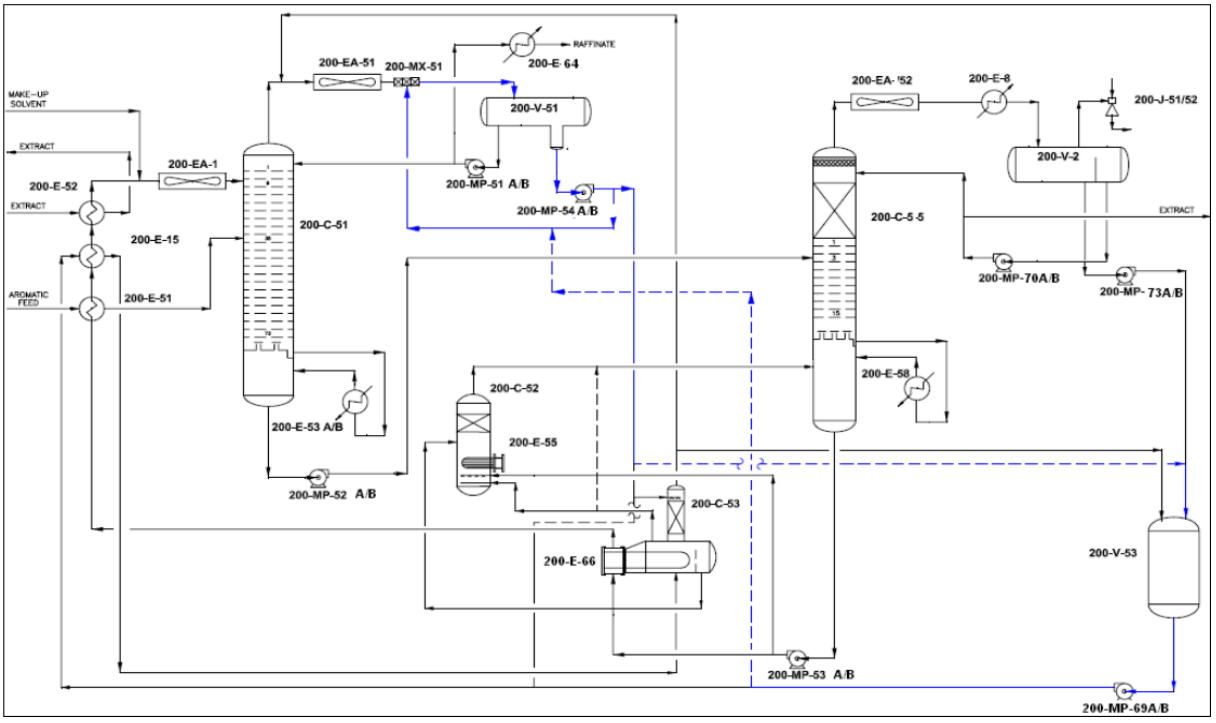


Figure II.3: *Water circulation loop* **[19].**

II.3.2. Fraction Section

II.3.2.1. Clay Treatment The aromatics extract product from the extraction section, stored in the clay tower charge tank 200-S-52, is pumped by the clay tower charge pump 200-MP-60 A/B, to the post-fractionation section, after being preheated in the extract preheater 200-E-52 against the hot lean solvent.

II.4. Factors Affecting Solvent Losses and Solvent Quality

- Degradation;
- Neutralization;
- Solvent losses in the raffinate;
- Solvent losses in the extract.

II.5. Factors Affecting Aromatics Purity and Recovery

The factors affecting aromatics recovery and purity at a given feed rate are **[19]**:

- Solvent rate and feed composition;
- ED Column – feed location;
- EDC bottom temperature;
- Water content in Solvent;
- Aromatic content in Solvent;
- Feed Temperature;
- Reflux Ratio;
- EDC operating pressure;
- Lean solvent temperature;
- Hydrocarbon content in lean solvent.

II.5.1. Solvent Rate and Feed Composition

The factors that primarily influence the recovery of aromatics are the composition of the feed and the solvent-to-feed ratio.

When the aromatic content in the feed increases, more aromatics dissolve in the solvent, resulting in a lower flow rate of raffinate.

In general, as the solvent-to-feed ratio increases at a given ratio, the volatility of the raffinate is reduced because more aromatics dissolve in the solvent **[20].**

To achieve the desired performance of the unit in terms of product purity and aromatic recovery, it is necessary to increase the solvent-to-feed ratio **[20].**

To demonstrate the influence of benzene content in the feed, a monitoring of the feed composition and benzene losses for a constant solvent-to-feed ratio of 1.05 allowed us to establish the following graph:

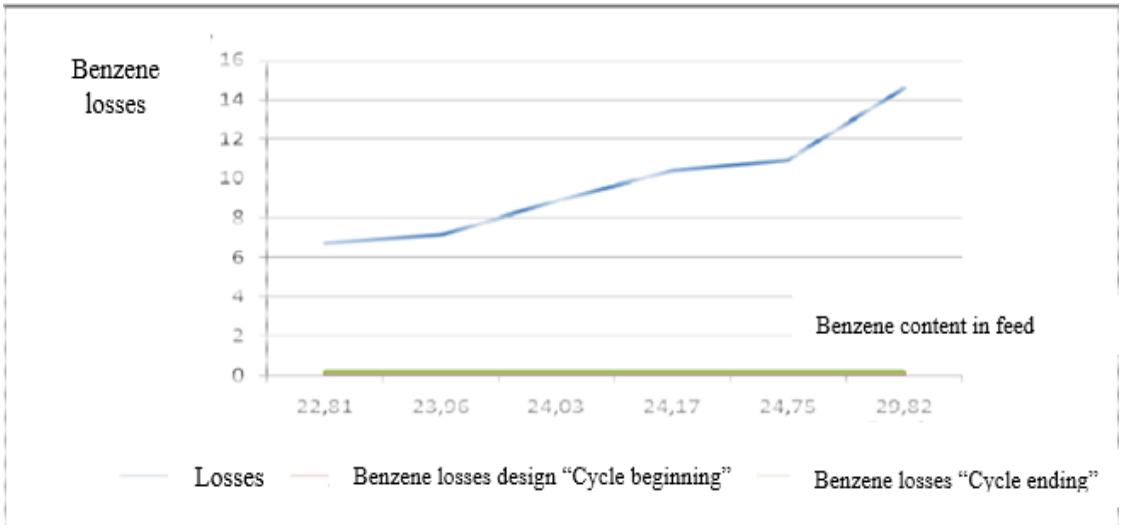


Figure II.4: *Losses variation depending on benzene content in feed.*

Benzene content in feed varies from day to day due to the operation of upstream units (Reforming / Reforming II) aimed at increasing the aromatic content in the naphtha.

- We observed that for a constant solvent-to-feed ratio, the losses increase with the increase in the benzene content of the feed.
- To understand the influence of the solvent-to-feed ratio.

Another monitoring was conducted using DCS data, which enabled us to establish the following graph:

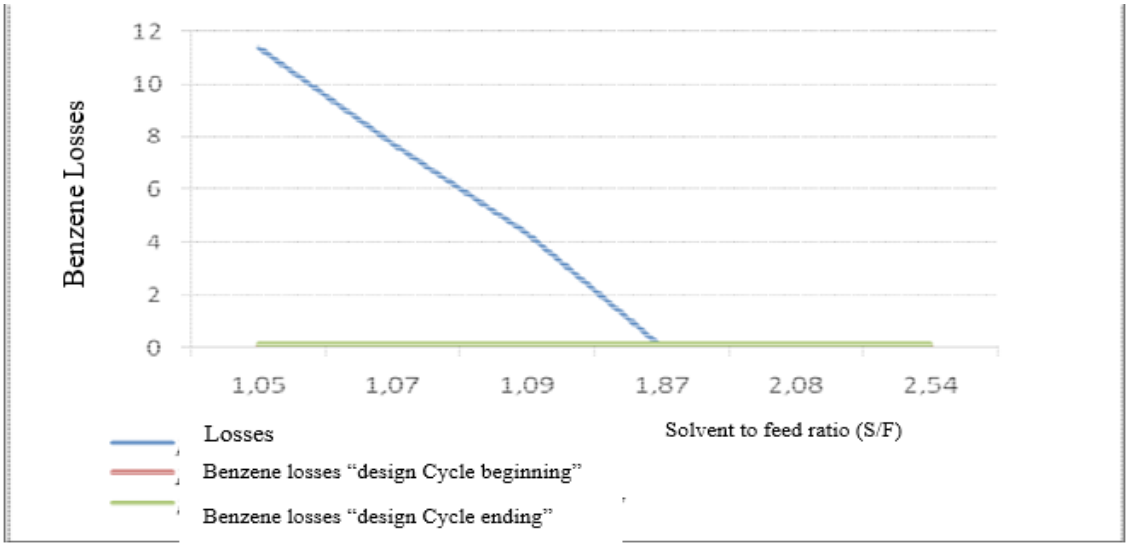


Figure II.5: *Benzene Losses variation depending on ration S/F.*

II.5.2. ED Column – Feed Location

With a fixed total number of stages, the feed point can be adjusted to vary the number of stages above and below the hydrocarbon feed in current operations to meet specific objectives of aromatic product purity and recovery **[20].**

Simply put, the stages above the feed operate to extract aromatics from the hydrocarbon phase, while the stages below the feed work to strip non-aromatics from the rich solvent. Generally, aromatic losses increase when there are fewer stages above the hydrocarbon feed point, while the purity of the extract increases with more stages below the hydrocarbon feed point. For a highly aromatic feed, more trays below the feed tray should be provided. Conversely, for a feed with low aromatic content, more trays above the feed tray should be provided **[20].**

Selectivity (product purity) is more critical than solubility (product recovery) for a high aromatic content in the feed, and it is the opposite for a low aromatic content in the feed. As a result, a feed with a high aromatic content requires more trays below the feed tray and fewer trays above the feed tray compared to a feed with low aromatic content. For this reason, the column has three feed inlets based on the aromatic content of the feed **[20].**

II.5.3. EDC Bottom Temperature

The benzene purity increases with higher than design EDC bottom temperature up to certain range. Typically, the benzene purity increases with higher bottom temperature at the cost of higher aromatic content in the raffinate.

A monitoring was conducted to examine the relationship between the column bottom temperature and benzene losses using the results from the reporting.

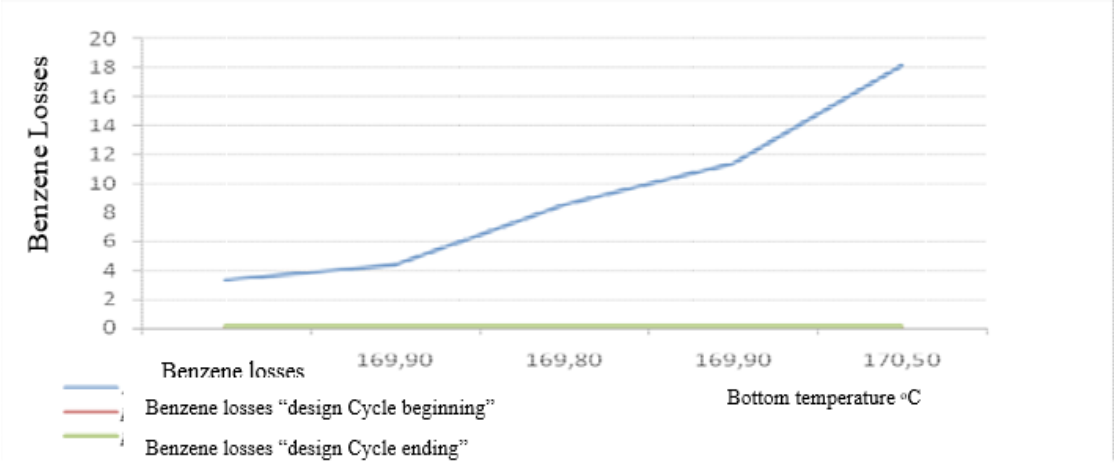


Figure II.7: *Losses variation depending on bottom temperature °C.*

We observed that for higher column bottom temperatures, aromatics tend to volatilize, which increases their losses in the raffinate.

II.5.4. Water Content in Solvent

The water content in the solvent is considered during solvent regeneration to maintain its viscosity.

The typical water content in the solvent is around 0.6-0.8% weight. A high amount of water in the solvent reduces the solubility of hydrocarbons, thereby decreasing aromatic recovery and increasing benzene losses **[22].**

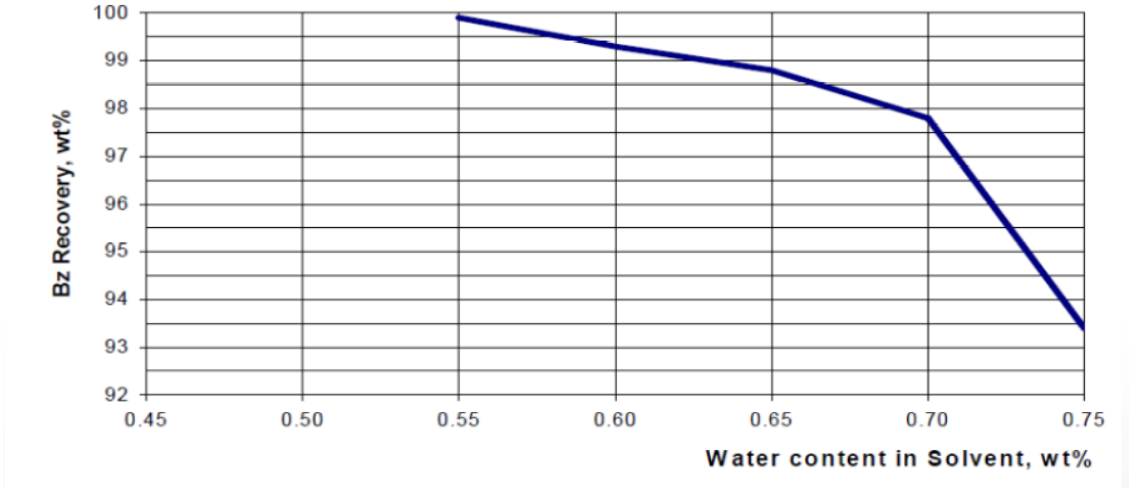


Figure II.8: *Benzene recuperation depending on water content in solvent.*

II.5.5. Feed Temperature

A monitoring using the data from the reporting allowed us to establish the following graph:

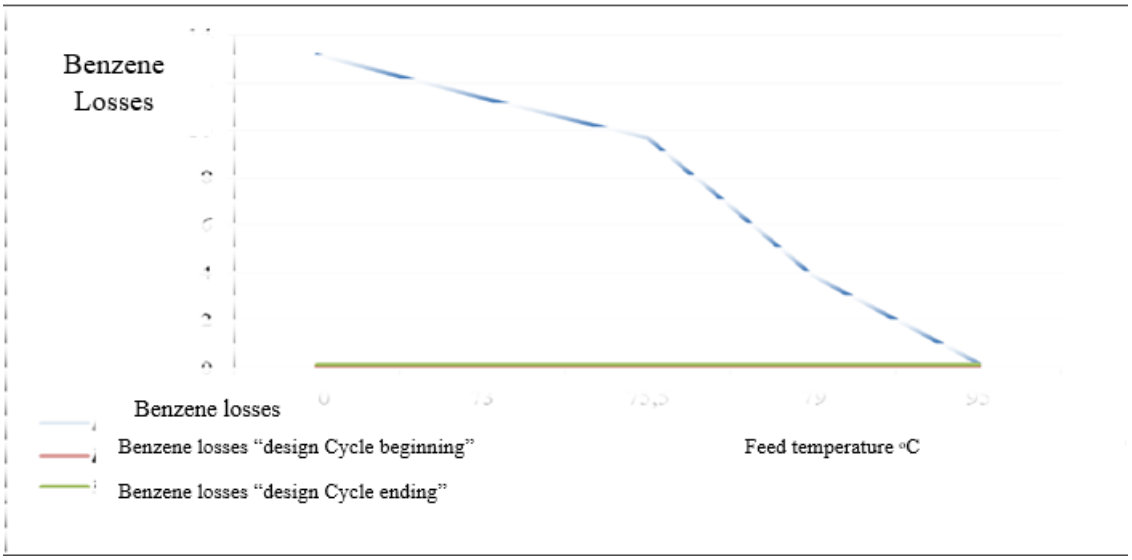


Figure II.8: *Benzene losses depending on feed temperature.*

In this graph, we observed that at a high feed temperature, the losses of benzene decrease.

II.5.6. Reflux Ration

A high reflux rate will reduce benzene losses as the incoming feed to the refinery will be reduced, and a large quantity will be reintroduced into the column. Using the data from the reporting, we establish the following graph.

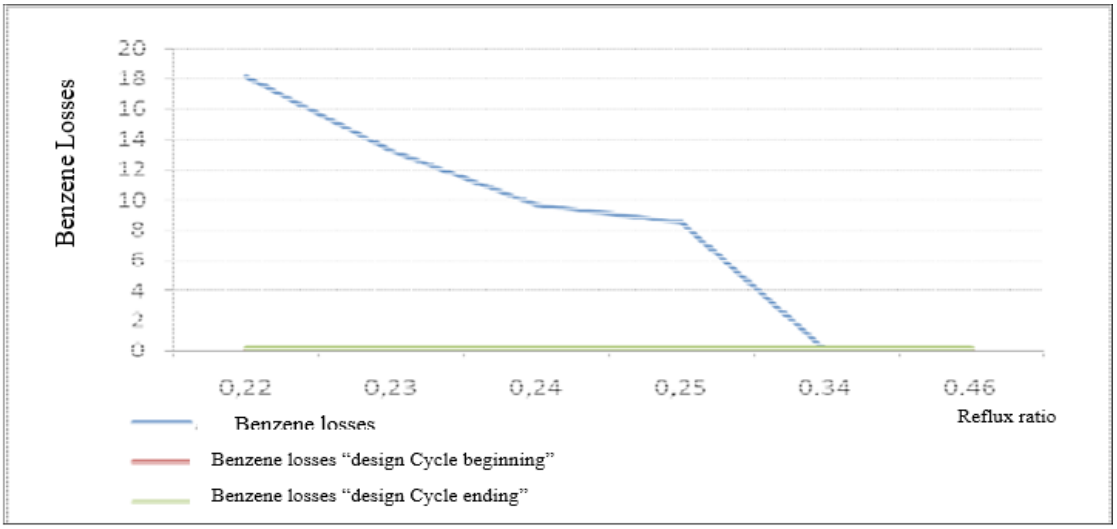


Figure II.10: *Losses variation depending on reflux ratio.*

II.5.7. EDC Operating Pressure

In general, as the EDC pressure is increased, the aromatic recovery may increase slightly, the aromatic purity decreases slightly, and the utility costs increase slightly

II.5.8. Lean Solvent Temperature

Solvent temperature entering the extractive distillation column is an important factor in controlling aromatic recovery. It also affects the temperature profile of the column as the solvent flow rate is significant. In general:

Increasing the solvent temperature will improve aromatic recovery due to increased solubility and reduced viscosity, which enhances mass transfer **[20].**

Data from the reporting has allowed us to study the variation in solvent temperature and its influence on benzene losses.

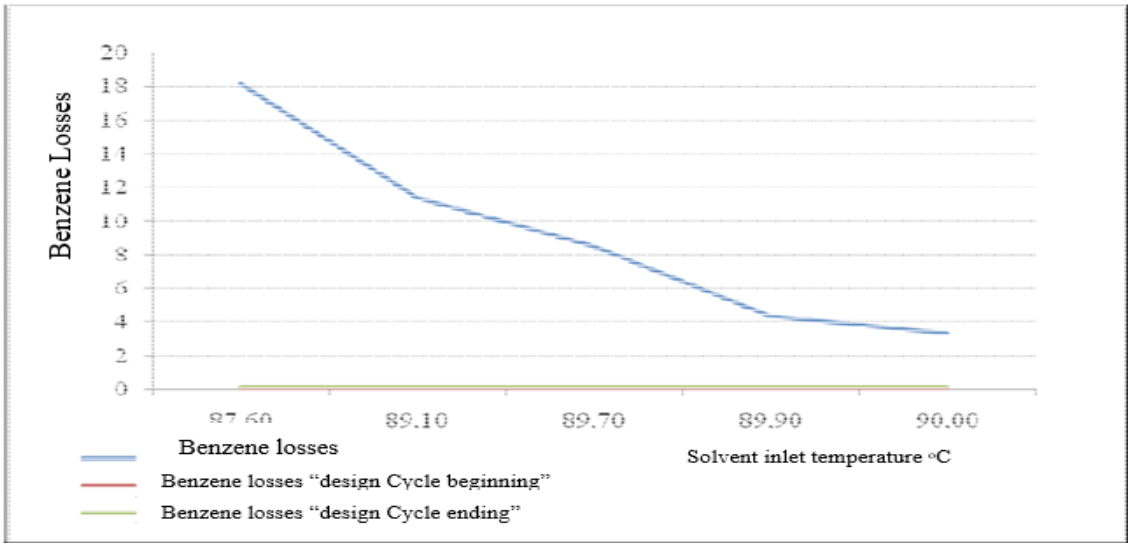


Figure II.11: *Benzene Losses variation depending on Solvent inlet temperature.*

II.5.9. Hydrocarbon Content in Lean Solvent

A high excess of hydrocarbons in the lean solvent will have a greater impact on the recovery of aromatics than the purity of the products in terms of quantity. If the lean solvent contains too many hydrocarbons, the aromatic compound "benzene" can be lost in the raffinate in the extractive distillation column **[20].**

The typical hydrocarbon content in the lean solvent is less than 1.0% by weight.

Aromatics that are not completely stripped in the stripping column (SRC) and remain in the solvent cause more significant losses in the extractive distillation column.

II.6. Factors Affecting Aromatics Recovery and Purity

The factors affecting aromatics recovery and purity at a given feed rate are:

- Solvent flow rate;
- EDC / SRC Pressure;
- Water content in Solvent;
- ED Column Feed Temperature;
- ED Column Bottom Temperature;
- Lean Solvent Temperature;
- Reflux Ratio.

Conclusion

Unit-200 produces high-purity benzene and toluene products, along with auxiliary products such as raffinate non-aromatic product. After undergoing extractive distillation and fractionation, the resulting products are collected in separate containers, ready for further processing or utilization in various industrial applications. These finished products are then sent to storage and made available at the battery limit for sale.

The efficiency of the extractive distillation process in terms of recovery and purity of aromatics is influenced by the process variables. These variables have a direct impact on the performance and effectiveness of the extractive distillation process.

Chapter III

Extractive Distillation Process

Introduction

Liquid-liquid extraction (LLE) and extractive distillation are two separation processes used in chemical industries. Liquid-liquid extraction involves transferring solutes between two liquid phases, while extractive distillation uses a solvent to enhance separation by altering vapor-liquid equilibrium. Both processes have distinct mechanisms and are chosen based on specific separation requirements. SONATRACH has decided to select the extractive distillation process (GTC) instead of the old process (LLE) during the renovation of Unit 200. This rehabilitation is based on a comprehensive study (operation, process, utility consumption, costs, and efficiency). In this chapter we make a comparison between two processes.

III.1. Extractive Distillation

Extractive distillation is a powerful technique utilized to separate close-boiling and azeotropic mixtures. As it gains wider consideration within industrial chemical processes, it is important to understand the inner workings and possible applications. Discussed here is an introduction to this technology and its corresponding mathematics, as well as examples that illustrate the use of extractive distillation in real-world applications **[21]**.

III.1.1. Introducing Extractive Distillation

Extractive distillation works by introducing a solvent to modify the molecular interactions of a mixture. The solvent alters relative volatilities by changing the intermolecular interactions of the components within the mixture. This ultimately allows one of the other components to be driven overhead as a distillate product with high purity **[22]**. Typically, the solvent added in extractive distillation has a higher boiling point than either of the feed components, and thus, is easier to recover for reuse. In azeotropic distillation, the solvent forms a new azeotrope with one of the components. Given the similarity with azeotropic distillation, extractive distillation was previously considered a special case of azeotropic distillation in a double-feed column, deemed suitable for the separation of close-boiling mixtures by using a solvent that would not form any new azeotrope **[23]**.

However, the two processes are now considered distinct since they obey different feasibility rules and operate using different column configurations. In addition, extractive distillation is easier to model via process simulations due to the absence of two liquid phases, normally present in azeotropic distillation. In this way, extractive distillation is often regarded as a preferable and easier method than azeotropic distillation.

III.1.2. The Process of Extractive Distillation

Extractive distillation involves at least two columns, depending on the complexity of the solvent recovery process. In the first column, there are two separate feeds. The "fresh feed," which contains the solution to be distilled, is added in the lower part of the column, and the solvent feed is added higher up in the column **[20]**.

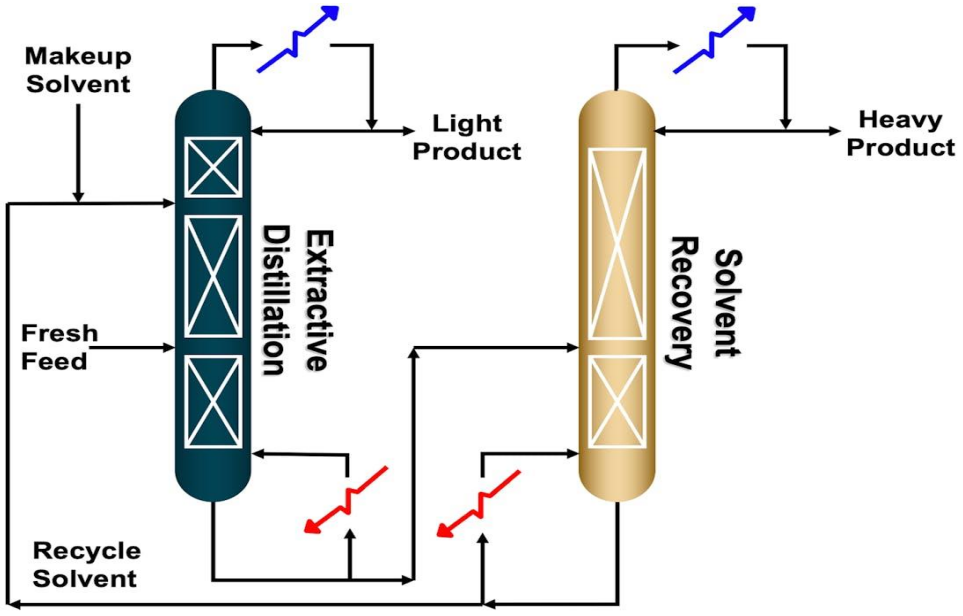


Figure III.1: *A simplified flow diagram for an extractive distillation process* **[21]**.

These feeds combine and are then processed through the three sections of the extractive distillation column: solvent recovery, rectifying and stripping (from top down). Solvent recovery refers to the trays between the solvent feed tray and the top of the column. This is where the component of higher relative volatility is concentrated and leaves as a distillate product. Reflux is required to separate it from the solvent and provide "reflux" to the rectifying section. Moving down the column, the rectifying section includes the trays between solvent feed and fresh mixture feed. In this section, the component of lower relative volatility is removed from the light component. The liquid and vapor composition at the top of this section is relatively free of the heavy component. Finally, the stripping section refers to the trays between the mixture feed tray and the bottom of the column. This is where the heavy component is concentrated and removed as the bottom's product. Both the heavy component and solvent are subsequently introduced into a recovery column in which the solvent is removed as the bottom's product and recycled back into the first column, and the distillate is relatively pure heavy component **[21]**.

III.1.3. Solvent Selection

When choosing a solvent for an extractive distillation process, its boiling temperature should ideally be higher than the "fresh feed" components. It should also be miscible with the mixture without forming an azeotrope. Additionally, it should alter the activity coefficients of the components, thereby causing their relative volatilities to change **[21]**.

When solvents are ranked in order of increasing relative volatility (or selectivity), the solvent ranked highest is typically considered to be the most promising solvent for a given separation task. From an economic viewpoint, this solvent will also always give the lowest total annual cost of the extractive distillation process **[21]**.

III.1.4. Advantages of Extractive Distillation

This technique offers several advantages over conventional distillation methods, and some of these advantages are as follows **[23,24]**:

- ✓ Enhanced Separation Efficiency: Extractive distillation can significantly improve the separation efficiency of a mixture compared to conventional distillation;
- ✓ Increased Purity: Extractive distillation enables the production of higher-purity products by effectively removing impurities or separating closely boiling components;
- ✓ Energy Efficiency: Extractive distillation can be more energy-efficient compared to alternative separation techniques;
- ✓ Process Intensification: Extractive distillation can lead to process intensification by enabling the achievement of desired separation objectives in a single unit operation.

III.2. Liquid-Liquid Extraction

Liquid-liquid extraction (LLE) is a mass transfer operation in which a solution (called the feed which is a mixture of a solute and a carrier liquid) is brought into intimate contact with a second immiscible or slightly miscible liquid (called the solvent) in order to achieve transfer of the solute(s) from the feed to the solvent. The two liquids phases that have different densities then are separated. The solute-rich phase (this is the solvent stream, now enriched with the solute) is called the extract; the residual feed stream that may have a little of the solute left in it is called the raffinate.

Solvent extraction is an important separation technique in petroleum refineries, particularly for lube oil production. The viscosity index (V.I.) is an important parameter for a lubricating oil. Many undesirable compounds, especially aromatics that reduce the V.I., have to be removed from the

lube oil feed stock to ensure the required viscosity index. BTX must also be removed from kerosene and jet fuels. This can be done conveniently by using a solvent selective for aromatics, sulphur, nitrogen, and oxygenated compounds. The main important solvents are furfural, sulpholane (tetrahydrothiophene-1,1-dioxide), N-methyl pyrrolidone (NMP), diethylene glycol, tetra ethylene glycol, methyl-ethyl-ketone (MEK), and methyl-isobutyl-ketone (MIBK) which selectively remove aromatics and weakly polar compounds (Lucan, 2000).

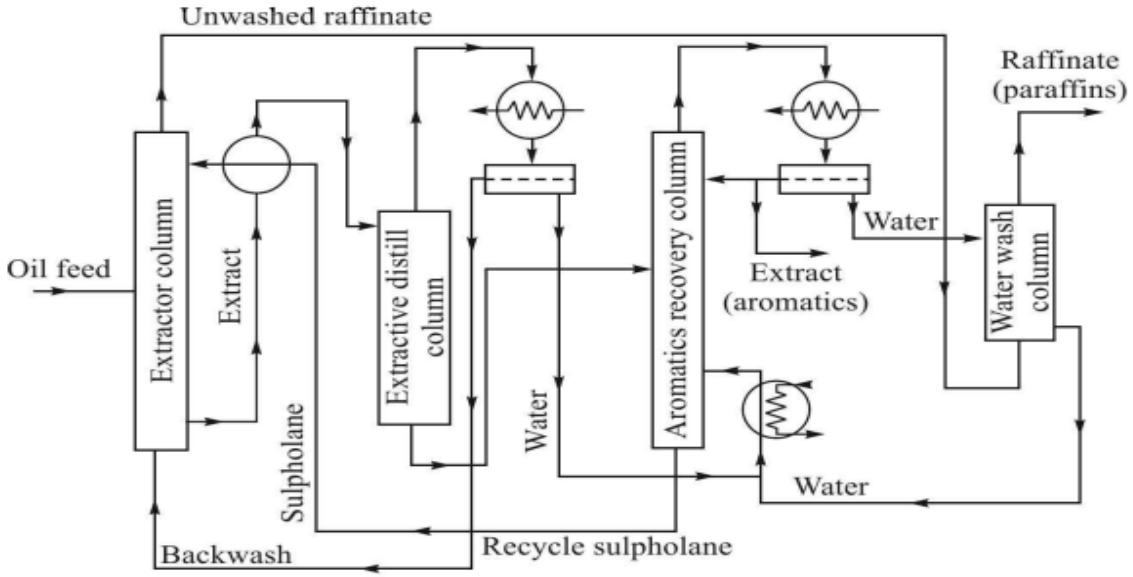


Figure III.2: *separation of aromatics from a feedstock- the sulpholane process* **[26].**

III.2.1. A few Applications of LLE

Solvent extraction has many other uses in food, pharmaceutical, metallurgical, environmental, and organic and inorganic chemical industries. It is used for purification of wet-process phosphoric acid to prepare the food-grade material. Recovery of acetic acid from a dilute aqueous solution has been practised since long because separation by distillation is very energy-intensive. Ethyl acetate and di-iso-propyl ether are the preferred solvents. Extraction of protein from ground fish or refining of fats by using propane as the purifying solvent are typical applications in the food industry. Natural vitamins A and D are extracted from fish liver oil using liquid propane **[26]**.

III.2.2. Limitations of LLE

Aromatics extraction processes have several limitations that can affect their efficiency and effectiveness. Some of the common limitations include **[27], [28], [29]:**

- ✓ **Selectivity:** Aromatic extraction processes may have limitations in achieving high selectivity for the target aromatic compounds. Depending on the extraction solvent and operating conditions.
- ✓ **Solvent Compatibility:** The choice of extraction solvent is crucial for achieving efficient separation. However, not all solvents are compatible with the aromatics or other components present in the mixture.
- ✓ **Energy Consumption:** Aromatics extraction processes can be energy-intensive, especially if additional steps such as solvent regeneration or solvent recovery are required.
- ✓ **Environmental Impact:** Organic solvents used in aromatics extraction processes can have environmental concerns due to their toxicity, flammability, or potential for emissions.
- ✓ **Process Optimization:** Extracting aromatics from complex mixtures can require optimization of various process parameters, such as solvent-to-feed ratio, temperature, pressure, and contact time.

III.3. Comparison Between Extractive Distillation and LLE

It is necessary for us to compare the new process with the old process. The following points have emerged as a result:

III.3.1. Number of Required Equipment

The extractive distillation technology only requires the operation of 2 columns instead of 5 in the case of liquid/liquid processes. The result is lower capital costs, a smaller footprint, and easier operation.

The equipment used in extractive distillation is reduced to two simple valve-tray distillation columns, which are easy to operate and require less maintenance. On the other hand, in the liquid/liquid extraction process, equipment such as extractors with rotating discs are characterized by lower reliability and require maintenance that is more extensive.

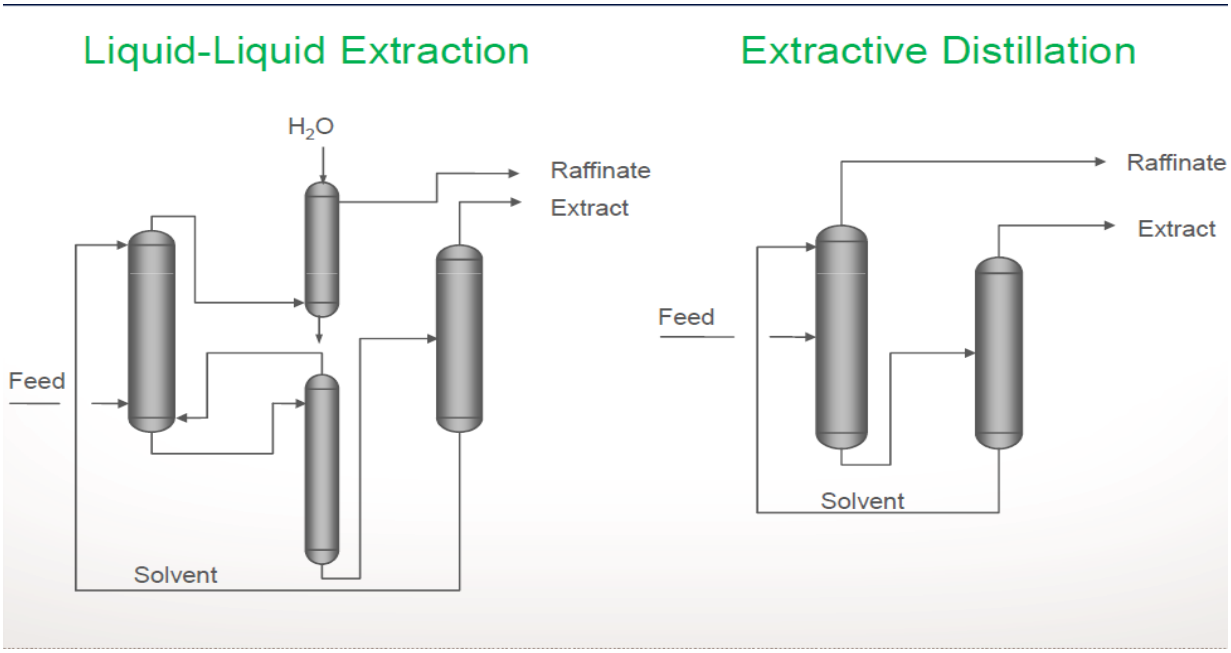


***Figure III.3**: The reduction in the number of columns by the new GTC process.*

III.3.2. Process Control

Extractive distillation is based on a vapour/liquid separation technique and provides flexibility to control critical process variables based on the DCS (Distributed Control System) in the control room. As a result, the start-up, operation, and shutdown procedures are simpler.

Therefore, the extractive distillation column contains only two phases: vapour at the top as a low-aromatic raffinate and liquid at the bottom as a high-aromatic extract. This simplifies the control of process parameters such as pressure, temperature, and flow rate.

The handling of the extractive distillation process remains simpler due to the inherent nature of distillation, which is well known and mastered by refinery operators and engineers.

The familiarity and expertise with distillation processes make it easier for operators and engineers to understand and manipulate the extractive distillation process. This level of understanding and mastery contributes to efficient control and operation of the unit.

III.3.3. Solvent Regeneration

The extractive distillation process incorporates solvent regeneration with a steam-stripping generator in the solvent regeneration column. This setup eliminates any operational continuity issues in the functioning of the unit, ensuring uninterrupted production without any shutdowns.

In contrast, the liquid/liquid extraction process is typically conducted in a batch-wise manner, which necessitates unit shutdowns during the extraction and solvent recovery stages. This intermittent operation can disrupt the production process and lead to downtime.

By integrating solvent regeneration within the extractive distillation process, the need for unit shutdowns is minimized, resulting in enhanced operational efficiency and continuous production.

III.3.4. Feed Stocks

The estimation of GTC (extractive distillation) shows that for the same oxygen content in the feedstock, it is approximately 100 times less corrosive compared to liquid/liquid extraction technologies.

Regarding composition, operability, and flexibility, the feedstocks are also important criteria for choosing and selecting the BTX recovery processes.

Liquid/liquid extraction is limited by the number of carbon atoms due to the solvent's inefficiency in effectively extracting heavier aromatic compounds in the liquid phase.

The Gt-BTX process does not have these limitations. Lighter components easily go to the raffinate stream without internal recirculation due to their high volatility. Heavier aromatic compounds are fully recovered despite their strong affinity for the solvent due to their lower boiling points.

In terms of the aromatic compound content of the feedstock, the liquid/liquid extraction (LLE) system cannot directly handle feedstocks with high concentrations of aromatics, as there would be no phase separation with feedstocks containing more than 75-80% aromatic compounds. On the other hand, with very low aromatic compound content, the solvent circulation rate in LLE systems becomes too high to be economical.

The Gt-BTX process, however, does not require phase separation and can efficiently operate across practically the entire range of aromatic compound content in the feedstock. It can effectively handle feedstocks with both high and low aromatic compound concentrations without the limitations faced by liquid/liquid extraction systems.

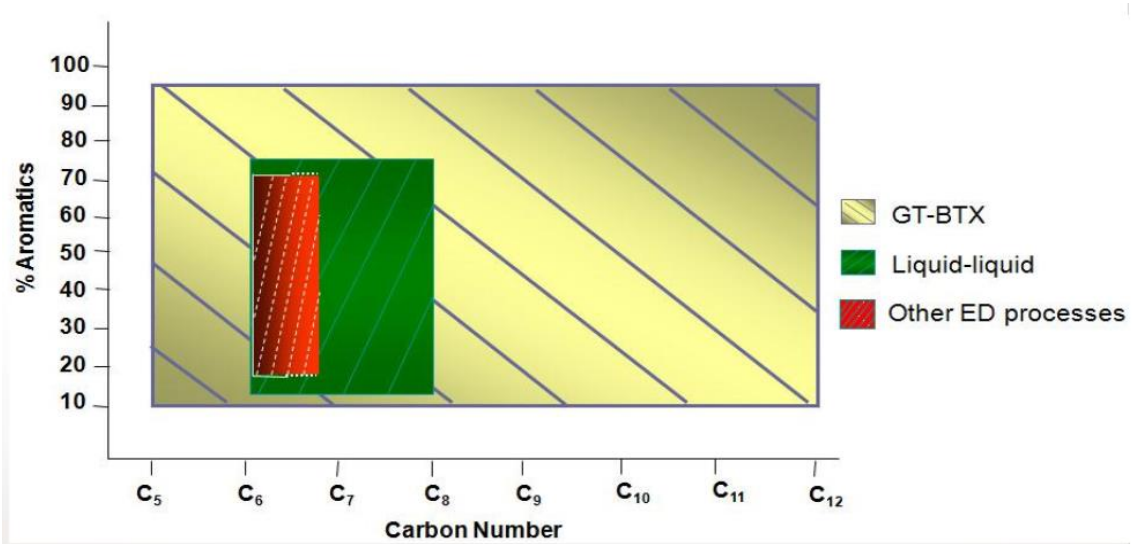


***Figure III.4**: Range of practical application according the nature of feedstocks.*

III.3.5. Comparisons With Other Extractive Distillation Solvents

Solvent	NC7/Benzene# (0.57 at 100C)
Techtiv-100$	2.44
Sulfolane	2.00
N-methylpyrolidone	1.95
N-formylmorpholine	1.89, 2.25&
Gylcol blends	1.35

Ref: GTC technology corporation
BP: NC7: 371.58 K(98.4), BZ:353.24 K(80.1)

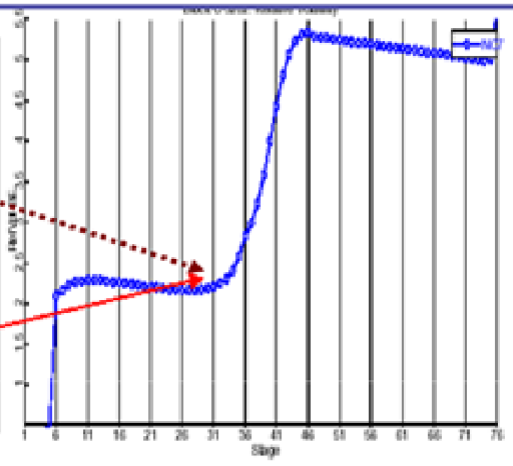


***Figure III.5**: Comparisons with other extractive distillation solvents.*

Commentary

When the value of relative volatility increased, the more efficient the separation becomes, requiring fewer treatment stages and fewer recycling loops.

#: Relative volatility of non-aromatic and aromatic components in the absence of a solvent.

$: The solvent used in the Gt-BTX process.

&: is the actual value of volatility in the extractive distillation process using N-formylmorpholine solvent.

III.3.6. Comparison of Utility Consumptions

The table below allows us to compare the two processes.

Table III.1: *Comparison of utility consumption between the two processes.*

Utility consumptions	Utilities			
	Vapour 30 bar t/h	**Cooling water**	**Fuel gas = (Enthalpy) Process kcal/h**	**Electricity**
Old process (Performance tests 1983) (production of 9000 tons per year of benzene)	20,221	182,6	3,36	427
New processes (Performance tests 2003) (production of 180000 tons per year of benzene)	41,1	1365	2,8	480

We preferred to compare two real cases: the first being the performance test of 1983, and the second being the projected consumptions for the new unit. Taking into account the difference in production capacity, which is higher than the initial capacity, we can reduce the impact of the reduction in energy consumption on the cost of production and therefore on the selling price. However, it should be noted that there is an increase in cooling water consumption due to the nature of the extractive distillation process, which is a thermochemical process conducted at higher temperatures than liquid-liquid extraction. Additionally, the consumption of fuel gas is higher in

the case of liquid-liquid extraction, primarily due to the number of equipment used, which requires a higher energy input.

III.3.7. Investment Cost

We conducted a preliminary comparison between the cost of a new extractive distillation unit and the cost of rehabilitating and refurbishing an existing liquid-liquid extraction unit. This comparison was done in order to assess the opportunity presented by rehabilitating our complex. The renovation of an existing unit is more financially advantageous than installing a new unit. The payback period is also shorter, making it more profitable. The renovation of existing facilities proves to be more cost-effective and undoubtedly saves time in the execution of the project.

Table III.2: *Comparison of investment costs between the two processes.*

	Extractive distillation	**Expansion of a liquid-liquid extraction unit**
Feed stocks	3500	4000
Installation cost (Millions of dollars)	6,5	3,5
Amortization period (Years)	2,2	1,2

III.3.8. GTC Compared to LLE System

Table III.3: *Comparison between GTC and LLE*

Item	**GT-BTX®**	**Liquid-Liquid Extraction**
Major unit operations	2	4
Capital cost	Base	Base plus 30-40%
Aromatics recovery	99.9%	<98%
Aromatics purity	99.99%	<99.9%
Energy consumption	Base	Base plus 20-30%
Feed flexibility	C_5-C_9	C_6
Process Control	Easy, Direct	Multiples Recycles
Solvent inventory	Base	Base +60%
Plot size	Base	Base +50%

III.3.9. Performances Comparison between The Two Processes

Since theoretical information alone is not sufficient to confirm the performance of a process (as in the case of liquid-liquid extraction where the unit ultimately failed to achieve the desired yields), we are interested in the actual performance of the extractive distillation process. The results are presented in the table below, which represents values from the operating log of a typical day with a 100% operating rate.

Table III.4: *The actual performance of the extractive distillation process.*

Parameter	Actual
EDC Feed Rate, Barrel per day	26,240
Benzene Purity, wt.%	99,99
Toluene Purity, wt.%	99,99
Benzene Recovery	99,99%
Toluene Recovery	99,99%
Xylene Recovery	100%
Solvent in the Raffinate,ppm	<1
Solvent in Extract, ppm **Aromatics in Raffinat3, wt.%**	<1 <0,01
Energy consumption	190

Table III.5: *The actual performance of the extractive distillation process.*

Item	GT-BTX®	Other ED Systems
Major unit operations	2	2-3
Capital cost	Base	Base plus 30%
Aromatics recovery	99.9%	<98%
Aromatics purity	99.99%	<99.9%
Energy consumption	Solvent system	Base plus 20-30%
Solvent system	Techtiv^{sm}-100	NFM, NMP - inferior
Product contamination	Negligible	Basic nitrogen, catalyst poison
Feed Flexibility	C5-C9	C6(7) only
Solvent inventory	Base + 30%	Base + 30%

We observe the actual performance of the unit, which is specific to the process that is unique in the world due to its simplicity, flexibility, high aromatic recovery rate, and especially its simplicity and lower production cost.

Conclusion

Both extraction and extractive distillation offer valuable means of separating mixtures, each with its own advantages and considerations. Understanding the differences between these techniques enables engineers and scientists to make informed decisions when designing separation processes.

The comprehensive study demonstrates the superior performance of the extractive distillation process, which led SONATRACH to choose it over the conventional extraction process. This decision was based on a thorough analysis of various factors.

Chapter IV

Application and Discussion

Introduction

The objective of this study is to employ Aspen HYSYS V12.1 software to simulate the extractive distillation section, mainly focusing on the extractive distillation column 51 (C-51). The ultimate goal is to identify optimal operating parameters that minimize the losses of benzene. To achieve this, the simulation will be divided into three stages.

- The first stage involves simulating the design case to confirm the suitability of the selected thermodynamic model and validate the accuracy of the simulation;
- The second stage involves simulating the real case, which will serve as great help to optimize the operating parameters;
- Finally, in the third stage, the operating parameters will be optimized to minimize losses in line with the design specifications. Overall, this study seeks to employ simulation techniques to optimize the extractive distillation process and reduce the loss of valuable product.

IV.1. Problem Description

The Extractive Distillation Column (EDC) is utilized to separate aromatics and non-aromatics using a highly selective solvent. By altering the relative volatility, the non-aromatic components are enhanced over that of aromatic components in the presence of a solvent (Techtiv-100^{SM}). This selective enhancement enables the non-aromatics to be distilled overhead, while the aromatics are recovered in the bottoms of the column.

In our practical stage, we have observed that the recorded benzene losses are significantly outside the design range. Despite the process equipment being fully functional, the actual losses in the unit have exceeded the expected range (0.07% to 0.16%) by far.

we will conduct a practical simulation of C-51 with the objective of determining the optimal operational conditions. The goal is to minimize the amount of benzene losses in the refinery stream, aligning with the design specifications.

IV.2. Introduction to The Simulator

IV.2.1. Simulation Definition

Chemical process simulation aims to represent a process of chemical or physical transformation through a mathematic model that involves the calculation of mass and energy balances coupled with phase equilibrium and with transport and chemical kinetics equations. All this is made looking for the establishment (prediction) of the behavior of a process of known structure, in which some preliminary data of the equipment that constitute the process are known.

IV.2.2. Applications of Process Simulation

Process simulation is a tool for process and chemical engineers that can be used in the execution of repetitive tasks or in activities of high complexity that must be solved in relatively short times. The various applications that process simulation has found are result of the necessity of:

- Making a better use of the energy resources;
- Minimizing the operating costs and the emission of waste streams;
- Increasing the yield and process efficiency;
- Improving the process controllability;
- Propelling the teaching of process design.

IV.2.3. Simulator Overview

IV.2.3.1. HYSYS History

HYSYS was created by a Canadian company called Hyprotech, founded by researchers from the University of Calgary. The first version of HYSYS, known as version 1.1, was published in 1996. Aspen Tech later acquired Hyprotech, including HYSYS, in May 2002. However, due to a ruling by the US Federal Trade Commission in 2004, Aspen Tech had to sell off Hyprotech's assets, including the HYSYS source code. Eventually, Honeywell bought these assets.

Aspen Tech have enhanced and modified HYSYS to suit the requirements of the industry **[30].**

IV.2.3.2. HYSYS Definition

Aspen HYSYS® is a chemical process simulator developed by Aspen Tech widely used to mathematically model chemical processes in an industrial level, especially in conceptual design and detailed engineering, control, optimization and process monitoring stages in a project. The most important applications of Aspen HYSYS® correspond to the industries of oil and gas processing, refineries, and some industries of air separation. All these practices take advantage of this simulator architecture that permits the integration of the steady-state and dynamic models in an only unit. In this way, it is possible to bring together the stages of process design with the rigorous analysis of the dynamic behavior and the control of the same, to evaluate in a direct way the effects that the decisions in the detailed design step have over the dynamic and controllability of the process **[31].**

IV.2.3.3. Process of Optimization

The optimization of chemical processes has a fundamental goal, which is the comparison of different alternatives to select the best according to some process response criteria. In an optimization process, it is important to identify the independent variables that lead to different results and make it possible to measure the dependent variables. It brings about the minimization of operating costs, energy consumption, and the maximization of yields and operational productivity **[31].**

IV.2.3.4. Simulation Methodology and Procedures

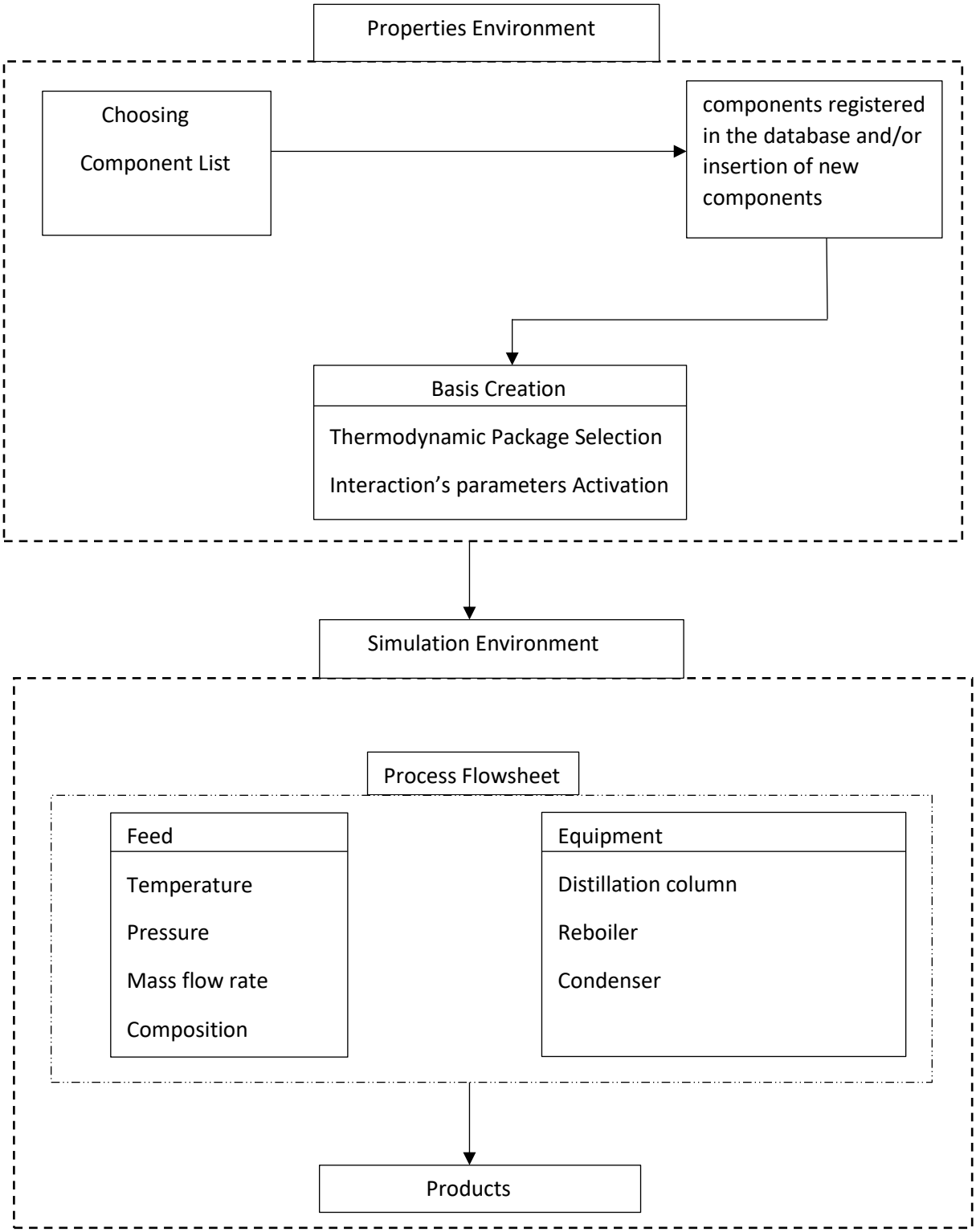


Figure IV.1: *process simulation steps using Aspen HYSYS.*

Before simulating in HYSYS, it is important to perform the following tasks:

- Clearly define the process, including all the relevant components, unit operations, and their interconnections;
- Collect all necessary data related to feed compositions, thermodynamic properties, physical properties, operating conditions, and any other relevant information required for accurate simulation;
- Select the appropriate thermodynamic models that accurately represent the behavior of the components in the system.

IV.2.3.5. Fluid Package Model

Universal QUAsi-Chemical (UNIQUAC) is a thermodynamic model developed by Abrams and Prausnitz in 1975. It uses the fraction of local surface area (θij) as a parameter to describe interactions between molecules in a mixture. Each molecule is characterized by two parameters: r (relative number of segments) and q (relative surface area).

UNIQUAC is comparable to the Wilson model and can determine liquid-liquid-vapor equilibrium.

This model satisfies thermodynamic consistency conditions, ensuring that the model calculations are physically meaningful and accurate. It takes into account the molecular interactions and provides reliable predictions of phase equilibria and separation efficiencies

The quality of the data of binary interaction is crucial in order to obtain sufficiently accurate results; in that sense a lot of attention must be paid during parameter regression **[31].**

IV.3. Monitoring Benzene Loss Variations Based on Operational Parameters

To better study the variation of the process parameters and their influence on the recovery of benzene, a monitoring was conducted using the data from the report (from the start-up until now). The table below shows the operational parameters of Unit 200:

Table IV.1: *Operational conditions and chromatographic analysis of different years.*

		Year 2013			Year 2014		
Operating condition	**Design**	**08/13/2013**	**08/14/2013**	**08/15/2013**	**06/01/2014**	**06/02/2014**	**06/03/2013**
Tº Top ºC	**89,1**	**93,1**	**94,7**	**94,7**	**92,5**	**93,1**	**93,1**
Tº Bottom ºC	**165**	**163**	**163,3**	**164**	**166,97**	**167,19**	**167,23**
Pº Top (kg/cm2_g)	**0,7**	**0,688**	**0,788**	**0,688**	**0,66**	**0,66**	**0,66**
Reflux	**0,34**	**0,29**	**0,26**	**0,25**	**0,281**	**0,2844**	**0,287**
% Benzene in the feed	**31,47**	**33,98**	**28,48**	**31,93**	**31,42**	**30,88**	**26,88**
Solvent/feed ratio	**1,66-2,5**	**1,65**	**1,65**	**1,65**	**1,07**	**1,07**	**1,07**
Tº inlet solvent ºC	**100-110**	**99**	**102,8**	**100**	**85,1**	**85,1**	**85,3**
Tº inlet feed ˚C	**93,4**	**95**	**95**	**95**	**70**	**70**	**70**
Benzene Losses %	**0,07-0,16**	**0,57**	**0,25**	**0,19**	**12,80**	**13,22**	**7,71**
		Year 2015			**Year 2016**		
Operating condition	**Design**	**10/30/2015**	**11/30/2015**	**12/30/2015**	**01/03/2016**	**01/03/2016**	**01/03/2016**
Tº Top ºC	**89,1**	**91,2**	**91,1**	**90,3**	**91,8**	**91,5**	**91,3**
Tº Bottom ºC	**165**	**168**	**170,5**	**159,1**	**169,9**	**169,8**	**169,9**
Pº Top (kg/cm2_g)	**0,7**	**0,619**	**0,608**	**0,618**	**0,63**	**0,63**	**0,63**
Reflux	**0,34**	**0,246**	**0,224**	**0,235**	**0,232**	**0,234**	**0,27**
% Benzene in the feed	**31,47**	**24,91**	**30,97**	**24,4**	**24,52**	**24,97**	**24,96**
Solvent/feed ratio	**1,66-2,5**	**1,02**	**1,18**	**1,04**	**1,05**	**1,09**	**1,09**
Tº inlet solvent ºC	**100-110**	**86,6**	**87,6**	**85,7**	**89,1**	**89,7**	**89,9**
Tº inlet feed ºC	**93,4**	**75,5**	**75,6**	**75,2**	**89,1**	**89,7**	**89,9**
Benzene Losses %	**0,07-0,16**	**9,68**	**18,15**	**3,82**	**11,4**	**8,51**	**4,33**
		Year 2017			**Year 2023**		
Operating condition	**Design**	**02/09/2017**	**02/09/2017**	**02/10/2017**	**05/22/2023**	**05/23/2023**	**05/24/2023**
Tº Top ºC	**89,1**	**92,2**	**91,2**	**90,8**	**90,9**	**90,9**	**90,68**
Tº Bottom ºC	**165**	**167,1**	**168,2**	**165,4**	**166,3**	**166,3**	**160**
Pº Top (kg/cm2_g)	**0,7**	**0,62**	**0,62**	**0,621**	**0,67**	**0,67**	**0,67**
Reflux	**0,34**	**0,22**	**0,20**	**0,22**	**0,14**	**0,14**	**0,4**
% Benzene in the feed	**31,47**	**31,98**	**28,28**	**27,21**	**21,02**	**21,04**	**21,04**
Solvent/feed ratio	**1,66-2,5**	**1,05**	**1,05**	**1,05**	**1,23**	**1,23**	**1,4**
Tº inlet solvent ºC	**100-110**	**93,2**	**90,8**	**90**	**88,4**	**88,4**	**88,4**
Tº inlet feed ºC	**93,4**	**72,5**	**72,3**	**72,4**	**84,6**	**84,6**	**84,6**
Benzene Losses %	**0,07-0,16**	**14,07**	**8,06**	**3,34**	**4,95**	**4,67**	**5,14**

Based on the monitoring history of Unit 200 after renovation, it is observed that benzene losses have significantly increased from 2013 to the current year (2023).

IV.4. Process Simulation

IV.4.1. Design Case Simulation

In this section, we will simulate C-51 using the design data and the operational parameters provided by the manufacturer.

The simulation of the design case will not only confirm the selection of the thermodynamic model but also validate the accuracy of the simulation.

IV.4.1.1. The Choice of The Thermodynamic Model

Extractive distillation involves complex interactions between multiple components and a solvent, making accurate prediction of phase equilibria essential for designing and optimizing the process. The chosen thermodynamic model is the UNIQUAC equation because it is the recommended model for multi-component extractive distillation.

IV.4.1.2. Simulation Procedure

a. Lunching

To begin, we launch the HYSYS software on the computer. Once HYSYS is launched, we create a new case by selecting "File" from the menu bar and clicking on "New Case." This will provide us with a blank canvas to start building our simulation.

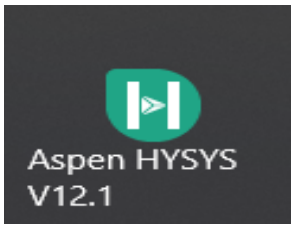


Figure IV.2: *Aspen HYSYS icon.*

b. Component List

We define the components of the EDC system by selecting "Components". We add the desired components required for our process.

We add all components as pure compounds except for the Techtiv-100^{SM} because it is not available in HYSYS databanks. We insert the solvent as a hypothetical component.

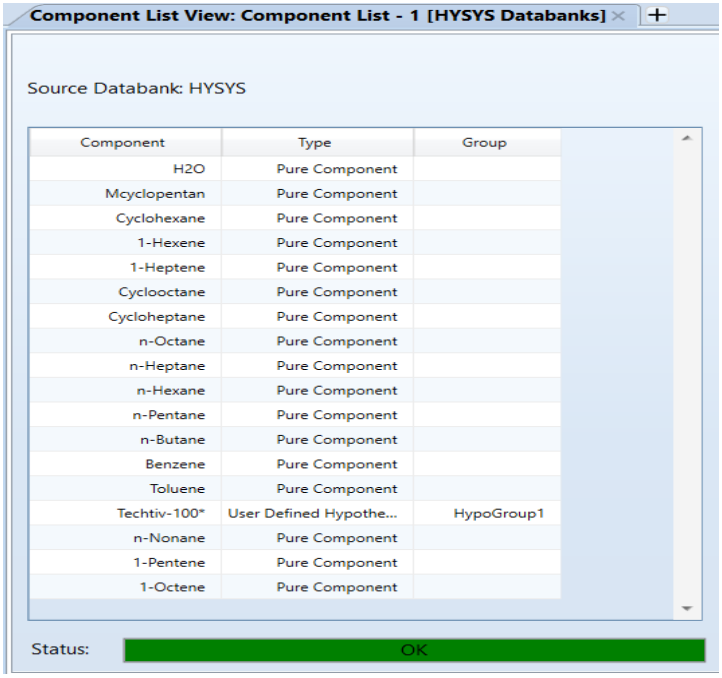


Figure IV.3: *Component List from Aspen HYSYS.*

c. Fluid Packages

We add the thermodynamic model we've chosen because it's recommended from the property package selection, it's under the name of UNIQUAC.

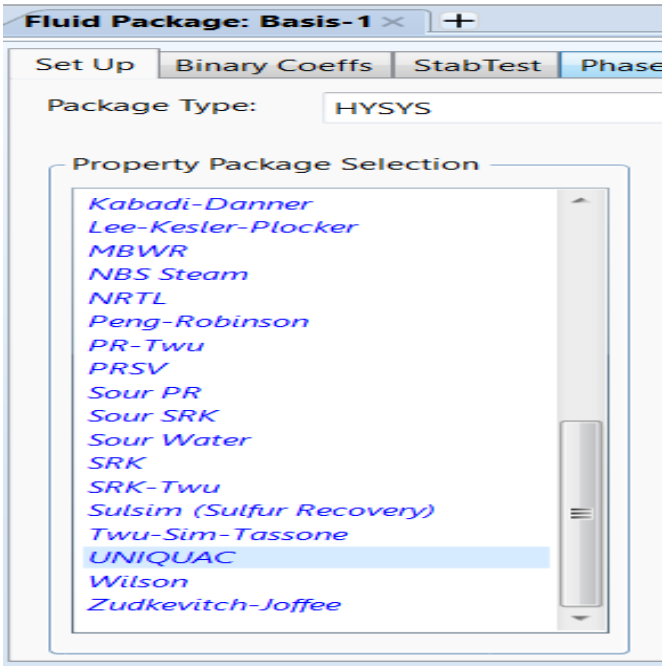


Figure IV.4: *Fluid Package Basis from Aspen HYSYS.*

d. Simulation Environment

It's the final step before converging our column, we build the process by dragging and dropping the distillation column from the model palette onto the canvas. Then we connect it by drawing streams to define the flow of material.

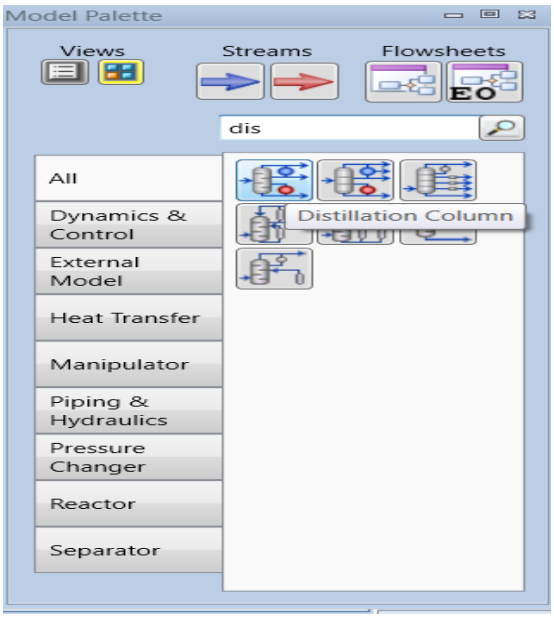


Figure IV.5: *Model Palette from Aspen HYSYS.*

After connecting the column with the material and energy streams, we proceed to specify its parameters and settings based on the data available from the stream summary.

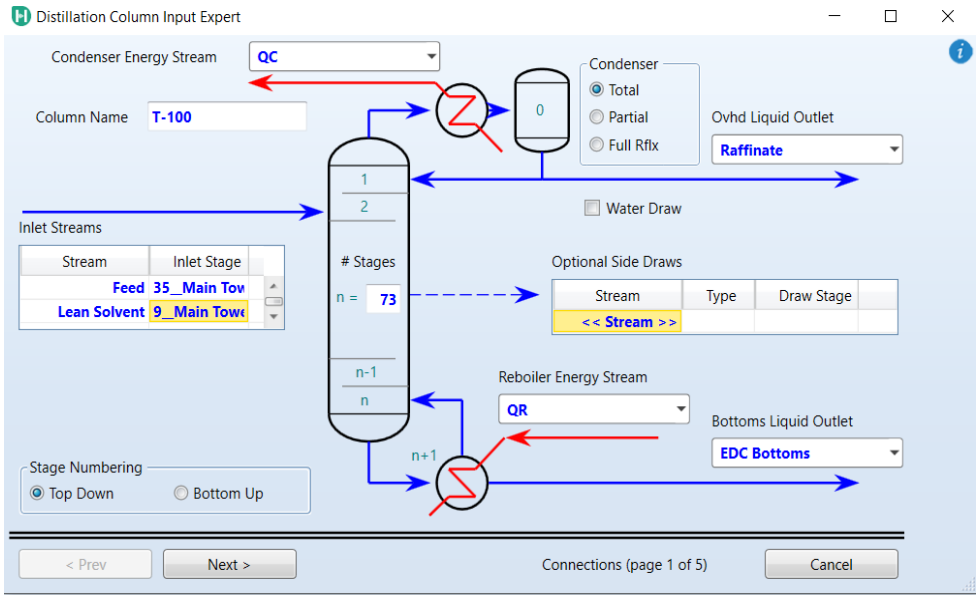


Figure IV.6: *Distillation Column Input page 1 from Aspen HYSYS.*

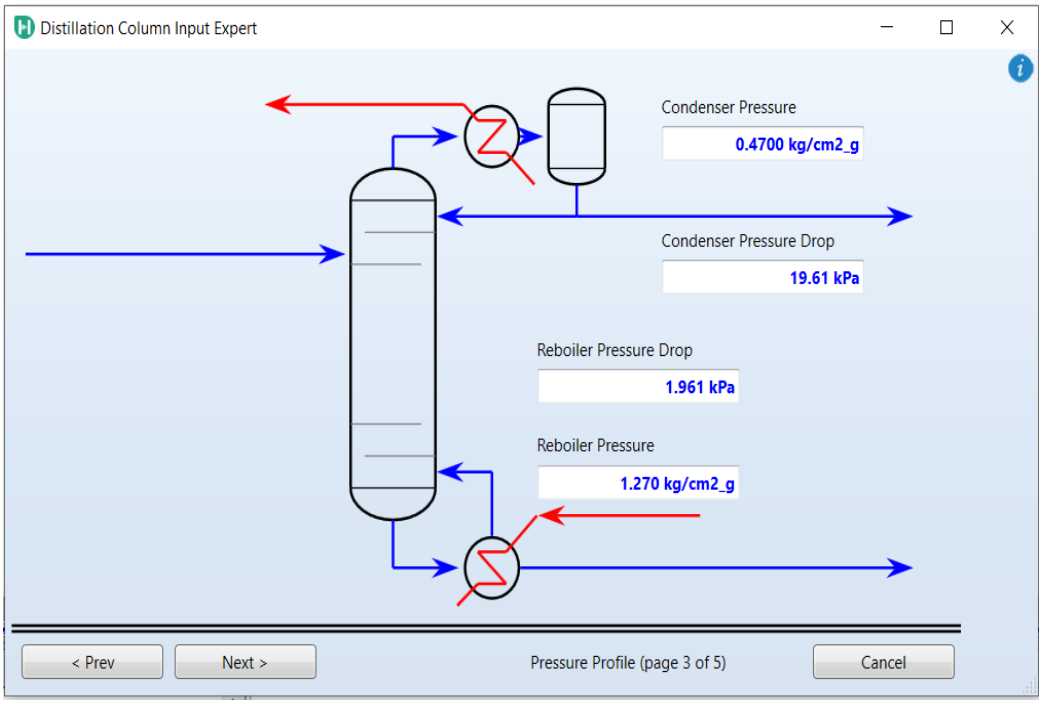


Figure IV.7: *Distillation Column Input page 3 from Aspen HYSYS.*

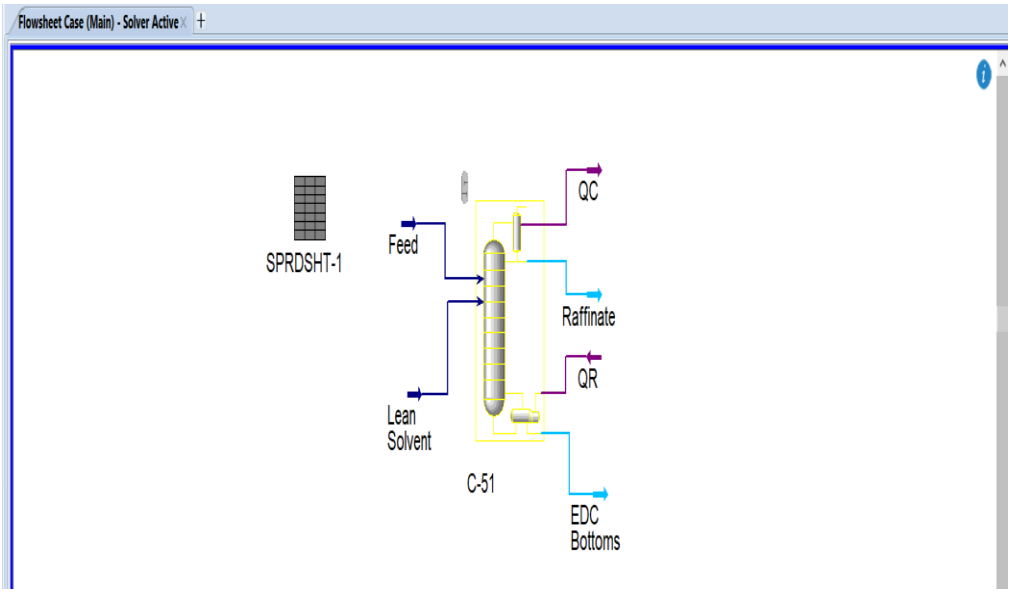


Figure IV.8: *Flowsheet Case before converging from Aspen HYSYS.*

In order to converge the column, we define the composition of both the feed and the lean solvent stream, we also have to define their properties and conditions by specifying the temperature, pressure, flow rate, and other relevant parameters for each stream, then we let HYSYS calculate the other undefined values.

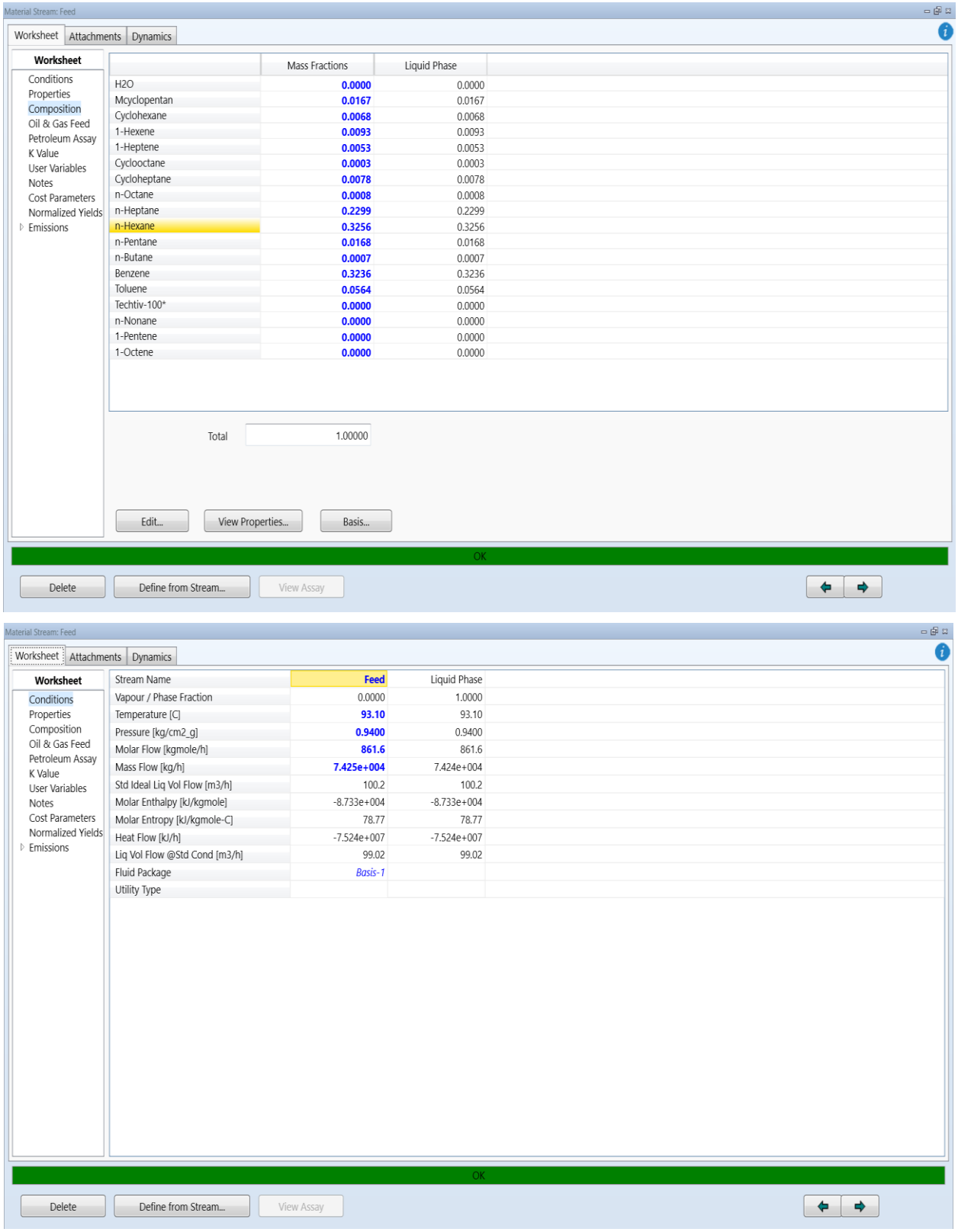


Figure IV.9: *Feed Stream composition and conditions from Aspen HYSYS.*

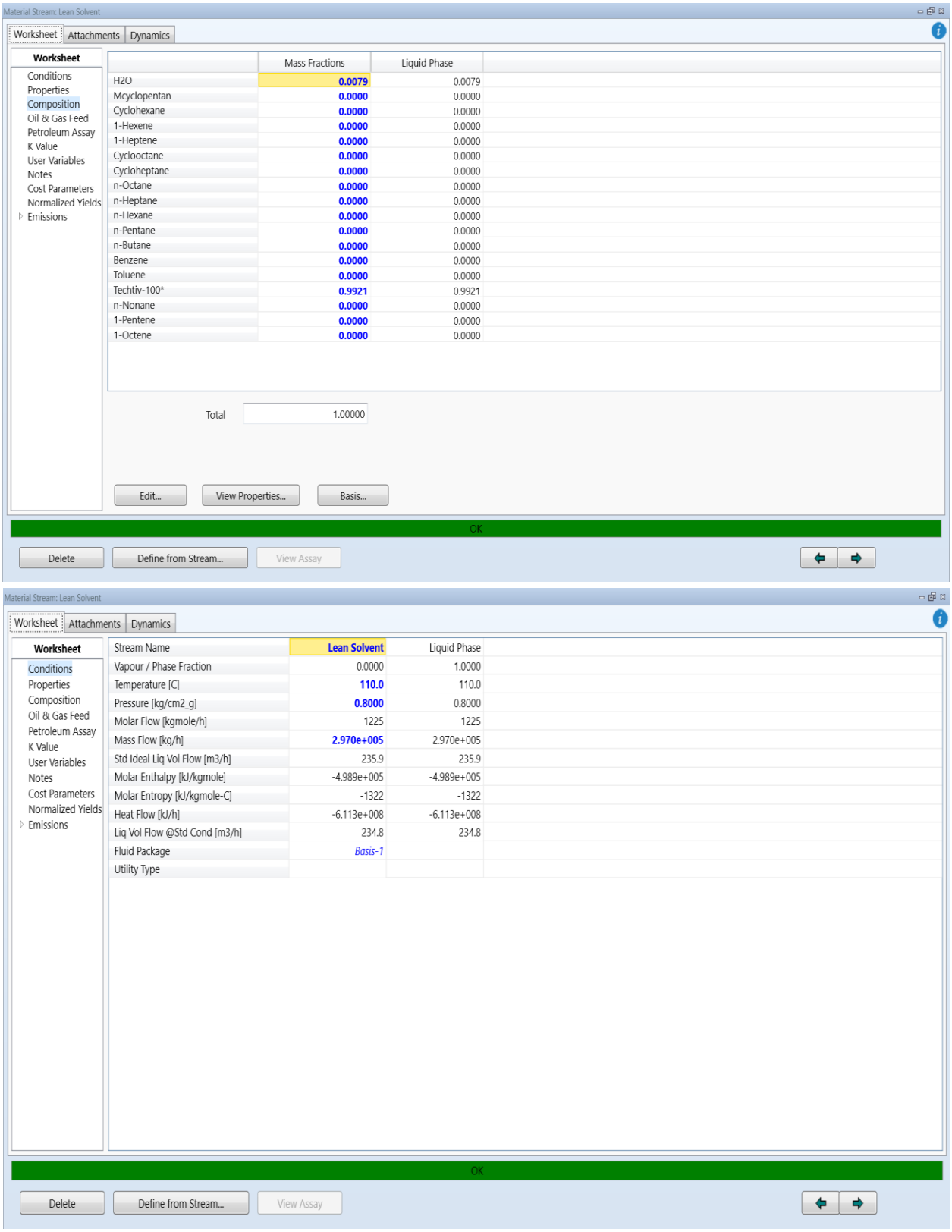


Figure IV.10: *Lean Solvent composition and conditions from Aspen HYSYS.*

Next, we head to the column again, accessing the monitor from the design list to add more specifications, such as distillate rate, reflux rate, and other known specifications.

It is essential to ensure that the degrees of freedom are equal to zero in order to proceed to the next step.

Finally, we run the simulation, it's going to take some time before it's successfully converged

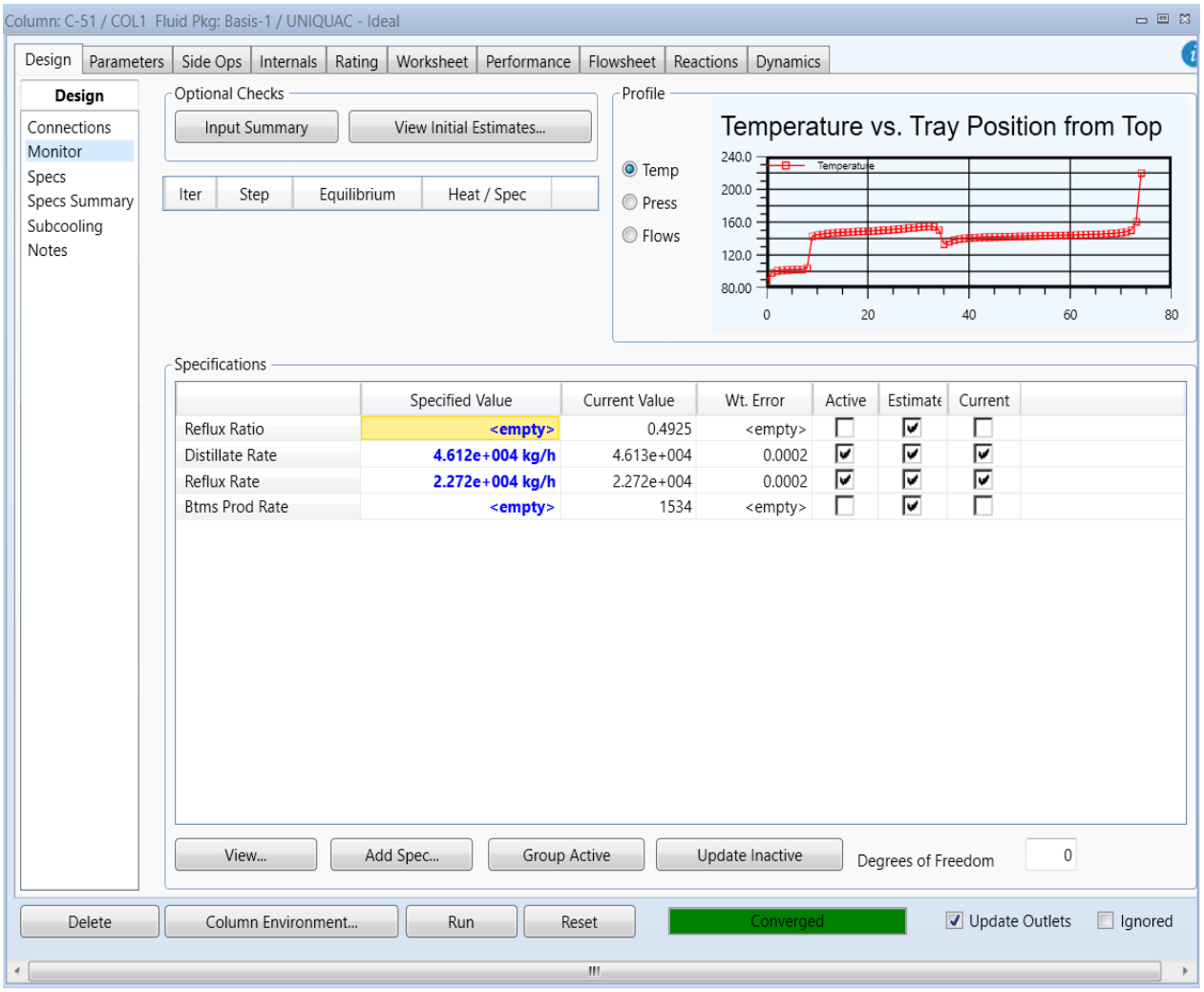


Figure IV.11: *Distillation Column Monitor C-51(Design Case) converged from Aspen HYSYS.*

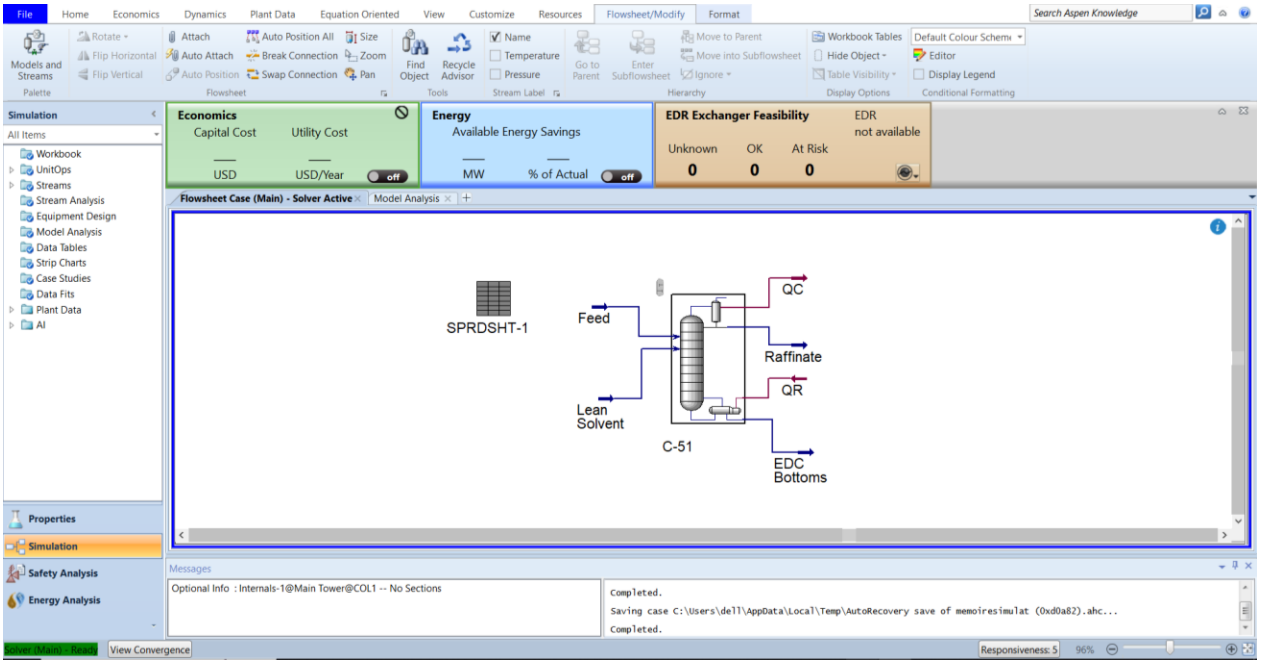


Figure IV.12: *Column C-51 converged from Aspen HYSYS.*

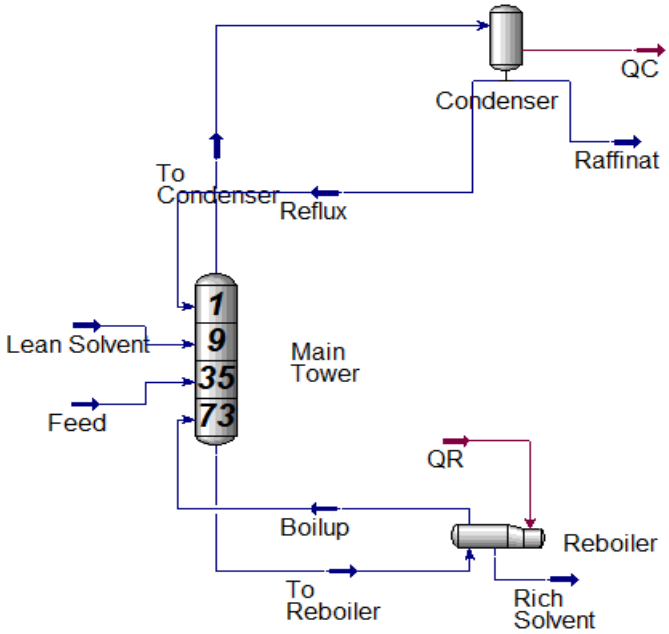
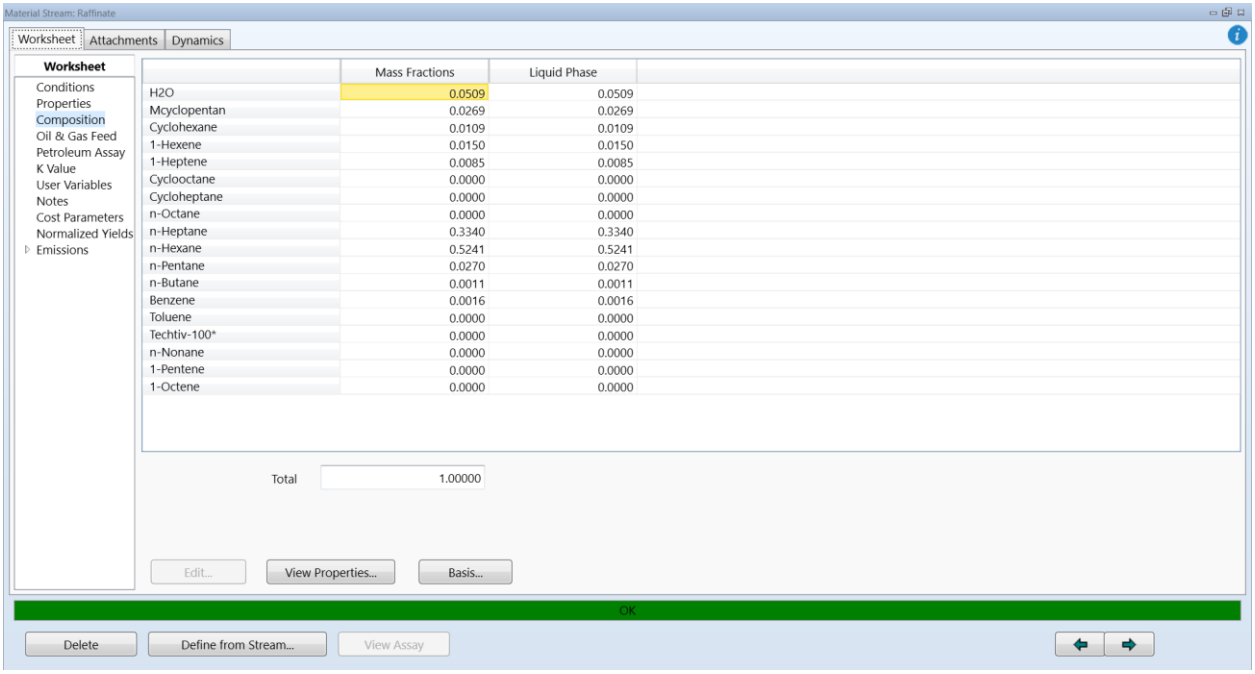


Figure IV.13: *Column C-51 Subflowsheet from Aspen HYSYS.*

To obtain results similar to the design, it is necessary to activate the interactions parameters.

IV.4.1.3. Design Case Simulation Results

In our simulation we're more focused on the benzene mass fraction in the raffinate, we obtain the following results:



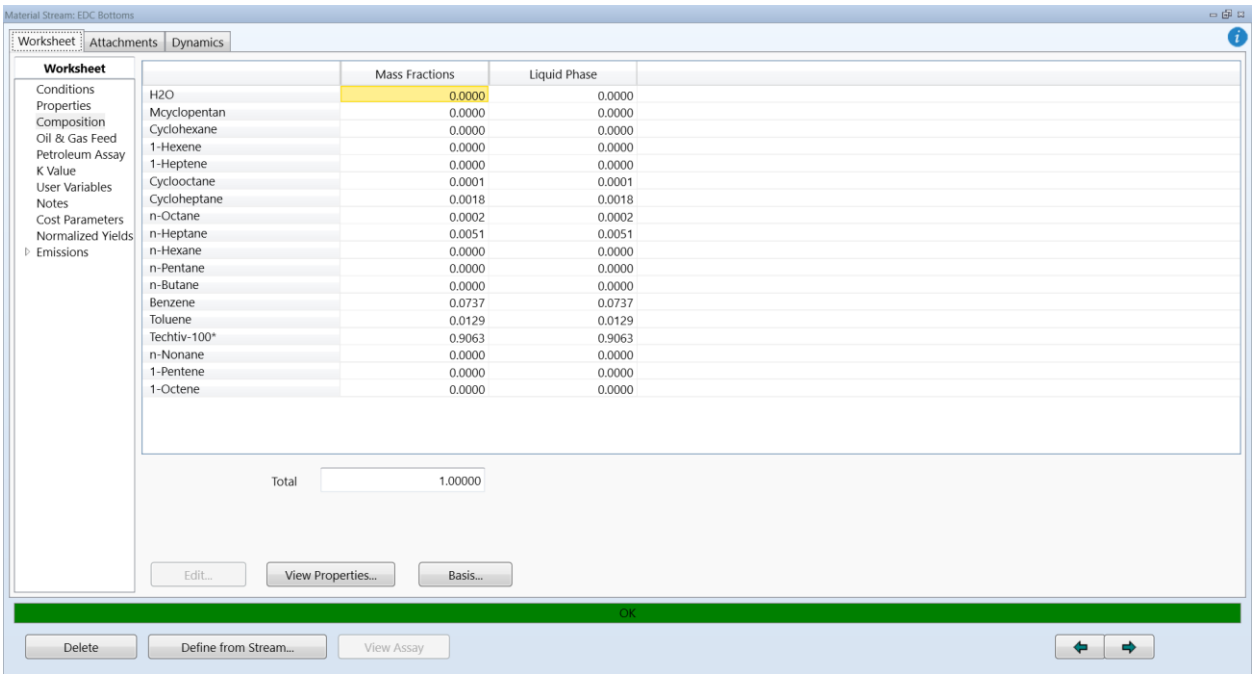


Figure IV.14: *Raffinate and EDC bottoms composition from Aspen HYSYS.*

IV.4.1.4. Results of The Design Case Simulation Compared to Manufacturer Data

To confirm the choice of the thermodynamic model, we compare the results provided by the HYSYS software to the design results in terms of flow rate and composition of both EDC bottoms and raffinate.

a. The Mass Flow Rates of The Raffinate and The Rich Solvent (EDC Bottoms)

Table IV.2: *Comparison between the mass flow rates obtained from the simulation and the design for the raffinate and rich solvent (EDC Bottoms).*

	Mass flow rate (Kg/h)	
	Design	Simulation
Raffinate	46118,00	46116,50
EDC Bottoms	323751,00	325128,87

We notice that the mass flow rates obtained from of the simulation are approximately close to the ones provided by the design, which confirms the thermodynamic model and indicates that both of the chosen model and simulation are accurate and reliable.

b. Raffinate Composition

Table IV.3: *Comparison of the raffinate composition between the simulation and the design.*

	Wt %	
	Design	Simulation
C4 Paraffins	0,09	0,11
C5 Paraffins	2,70	2,70
C6 Paraffins	52,42	52,41
C7 Paraffins	37,01	33,40
C8 Paraffins	0,14	0,00
C9 Paraffins	0,00	0,00
C5 Olefins	0,00	0,00
C6 Olefins	1,50	1,5
C7 Olefins	0,86	0,85
C8 Olefins	0,00	0,00
MCP	2,69	2,69
C6 Naphthenes	1,10	1,09
C7 Naphthenes	1,26	0,00
C8 Naphthenes	0,05	0,00

C8 Aromatics	0,00	0,00
Benzene	0,16	0,16
Toluene	0,00	0,00
Techtiv-100	0,00	0,00
Water	0,03	5,09
TOTAL	100	100

We notice that the values obtained through simulation closely resemble the manufacturer's data, this further confirms the selected thermodynamic model and the simulation accuracy.

c. Rich Solvent (EDC Bottoms) Composition

Table IV.4: *Comparison of the rich solvent composition between the simulation and the design.*

	Wt %	
	Design	Simulation
C4 Paraffins	0,00	0,00
C5 Paraffins	0,00	0,00
C6 Paraffins	0,00	0,00
C7 Paraffins	0,00	0,51
C8 Paraffins	0,00	0,02
C9 Paraffins	0,00	0,00
C5 Olefins	0,00	0,00
C6 Olefins	0,00	0,00
C7 Olefins	0,00	0,00
C8 Olefins	0,00	0,00
MCP	0,00	0,00
C6 Naphthenes	0,00	0,00
C7 Naphthenes	0,00	0,18
C8 Naphthenes	0,00	0,01
C8 Aromatics	0,00	0,00
Benzene	7,40	7,37
Toluene	1,29	1,29
Techtiv-100	91,01	90,63
Water	0,29	0,00
TOTAL	100	100

We notice that the values provided by the manufacturer and those obtained from the simulation are very close, which again confirms the choice of the thermodynamic model. the simulation results are almost identical to the design data.

IV.4.2. Real Case Simulation

Once the thermodynamic model selection is confirmed, we will proceed by simulating a real case, taking into account the changes in feed and the applied operating conditions. This aims to evaluate the possibility of reducing losses in Benzene.

The data utilized for this simulation corresponds to a real case from the year 2023.

IV.4.2.1. Feed Composition

The feed used is based on the analysis reports from the laboratory of Skikda refinery (RA1K). (**Table IV.5)** shows the comparison between the composition of the feed on 05/24/2023 and the composition of the design feed.

Table IV.5: *Comparison of the feed composition between the real case of 05/24/2023 and the design.*

	Wt %	
	Design feed composition	Real case feed composition (05/24/2023)
C4 Paraffins	0,06	0,04
C5 Paraffins	1,68	7,01
C6 Paraffins	32,56	42,11
C7 Paraffins	22,99	21,50
C8 Paraffins	0,08	0,00
C9 Paraffins	0,00	0,00
C5 Olefins	0,00	0,10
C6 Olefins	0,93	0,33
C7 Olefins	0,53	0,21
C8 Olefins	0,00	0,00
MCP	1,67	1,83
C5 Naphthenes	0,00	0,06
C6 Naphthenes	0,68	0,00
C7 Naphthenes	0,78	0,68
C8 Naphthenes	0,03	0,00
C8 Aromatics	0,00	0,00
Benzene	32,36	21,04
Toluene	5,64	5,19
Water	0,00	0,00
TOTAL	100	100

We notice that there's a significant difference between the feed compositions in both cases, which leads to a modification of the operating parameters.

IV.4.2.2. Simulation

To simulate the real case, we follow the previous steps we took during the design phase, incorporating changes to the operating parameters, inlet composition, and conditions.

We obtain convergence in the real case column:

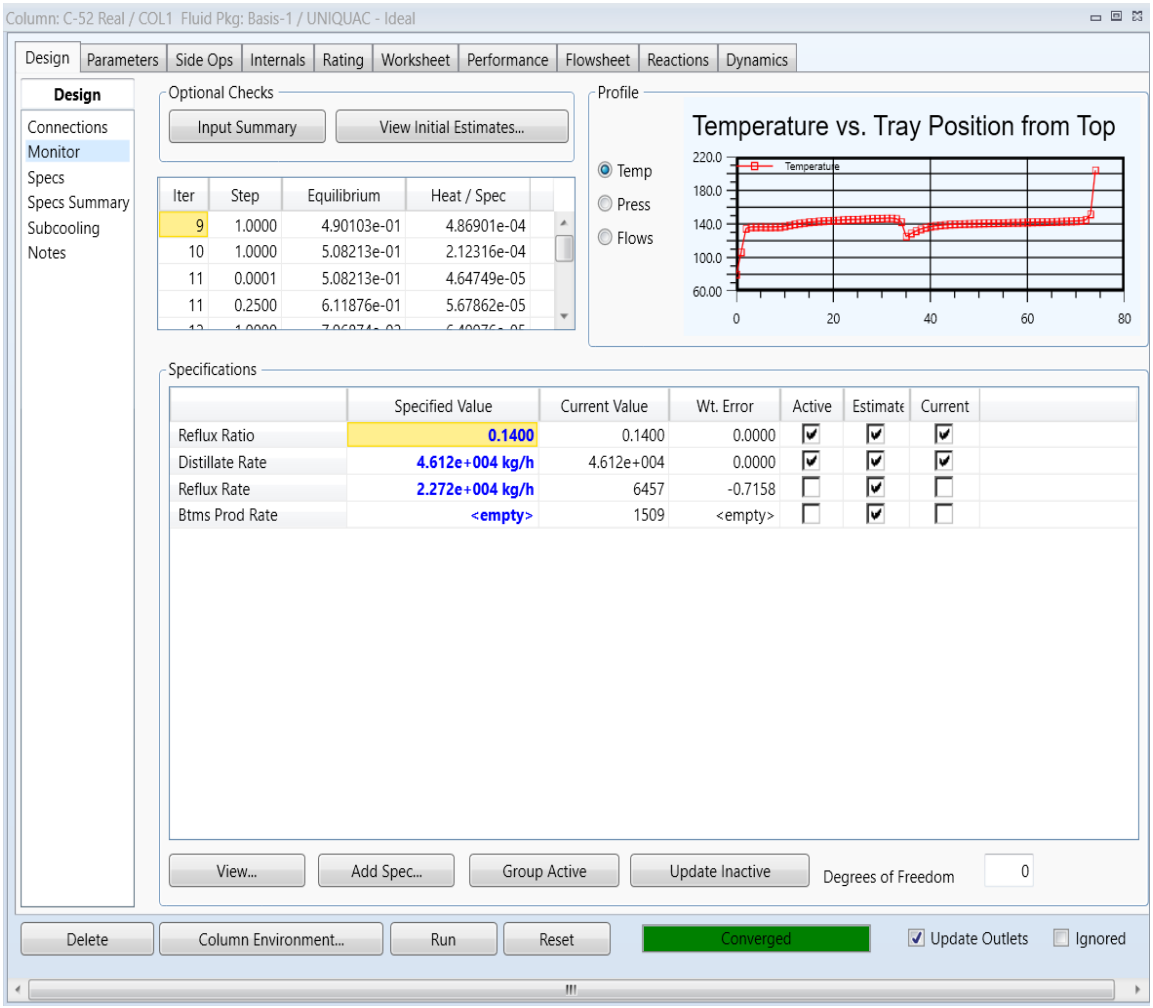


Figure IV.15: *Distillation Column Monitor C-51(Real Case) converged from Aspen HYSYS.*

IV.4.2.3. Real Case Simulation Results

a. Raffinate Composition

In our simulation we're more focused on the benzene mass fraction in the raffinate.

After completing the simulation, we obtained the following results:

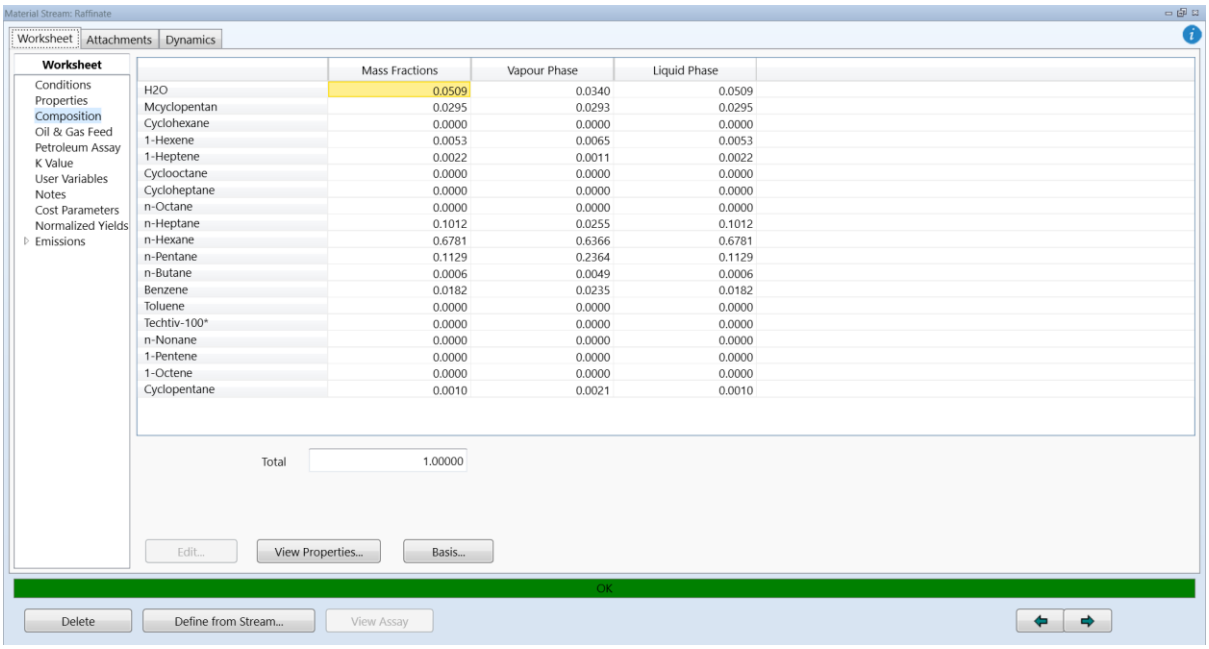


Figure IV.16: *Raffinate composition (Real Case) from Aspen HYSYS.*

IV.4.3. Comparison Between Real Case and Design Case

We conducted a comparison between the benzene losses in the real case and the simulation, aiming to showcase the substantial disparity between the two.

Table IV.6: *Comparing the benzene losses among the design case, the real case, and its simulation.*

	Design	**Case 05/24/2023**	**Case 05/24/2023 simulation**
Benzene in the Raffinate %	0,16	5,14	1,82

Table IV.7: *Real case simulation results and the operating conditions.*

Operating conditions	**design**	**05/22/2023**	**05/23/2023**	**05/24/2023**	**05/24/2023 Simulation**
Tº Top ˚C	89,1	90,9	90,9	90,9	90,68
Tº Bottom ˚C	165	166,3	166,3	166,3	162
Pº Top (kg/cm²_g)	0,7	0,67	0,67	0,67	0,67
Reflux	0,34	0,14	0,14	0,14	0,14
%Benzene in the feed	32,36	21,02	21,21	21,04	21,04
Solvent/Feed ratio	1,66-2,5	1,23	1,23	1,23	1,23
Tº inlet solvent ˚C	100-110	88,4	88,4	88,4	88,4
Tº inlet feed ˚C	93,1	84,6	84,6	84,6	84,6
Benzene Losses %	0,07-0,16	4,95	4,67	5,14	1,82

In the real case, comparing the results of the raffinate composition between HYSYS simulation and design analysis shows that the results are close. However, when comparing the simulation with chromatographic analysis and the operating parameters, a significant discrepancy is observed in the benzene values.

IV.4.4. Optimization

To optimize the process, our primary focus should be on applying modifications to the process variables/parameters that directly affect the aromatics recovery and purity.

by actively adjusting and optimizing these variables, we can enhance the efficiency of the extraction process and achieve higher levels of aromatics recovery and purity.

In this section, our focus is on optimizing the operating parameters of the EDC column to minimize losses. To accomplish this, we have selected the previously studied case of 05/24/2023 and made modifications to the EDC column parameters in the HYSYS simulator.

The main purpose of these modifications is to bring benzene losses closer to the design range, which falls within the interval of 0.07% to 0.16%.

By adjusting the parameters of the EDC column, our objective is to optimize its performance in order to reduce benzene losses and maintain stable operation.

IV.4.4.1. The Feed Location Influence

We maintain the same operating parameters throughout the process simulation, making changes only to the feed inlet stage. Starting from a lower stage, stage 31, we progressively move upwards until stage 39. By doing so, we aim to achieve improved results in terms of separation efficiency.

The table below displays the results obtained from the simulation:

Table IV.8: *Results of optimizing the feed stage inlet.*

Operating conditions	design	Case 1	Real case	Case 2	Case 3
Feed Location	35	31	35	37	39
Tº Top ˚C	89,1	90,1	90,68	90,74	90,85
Tº Bottom ˚C	165	161,90	162,30	162,30	162,40
Pº Top (kg/cm^2_g)	0,7	0,67	0,67	0,67	0,67
Reflux	0,34	0,14	0,14	0,14	0,14
%Benzene in the feed	32,36	21,04	21,04	21,04	21,04
Solvent/Feed ratio	1,66-2,5	1,3	1,3	1,3	1,3
Tº inlet solvent ˚C	100-110	88,4	88,4	88,4	88,4
Tº inlet feed ˚C	93,1	84,6	84,6	84,6	84,6
Benzene Losses %	0,07-0,16	2,07	1,82	1.75	1,69

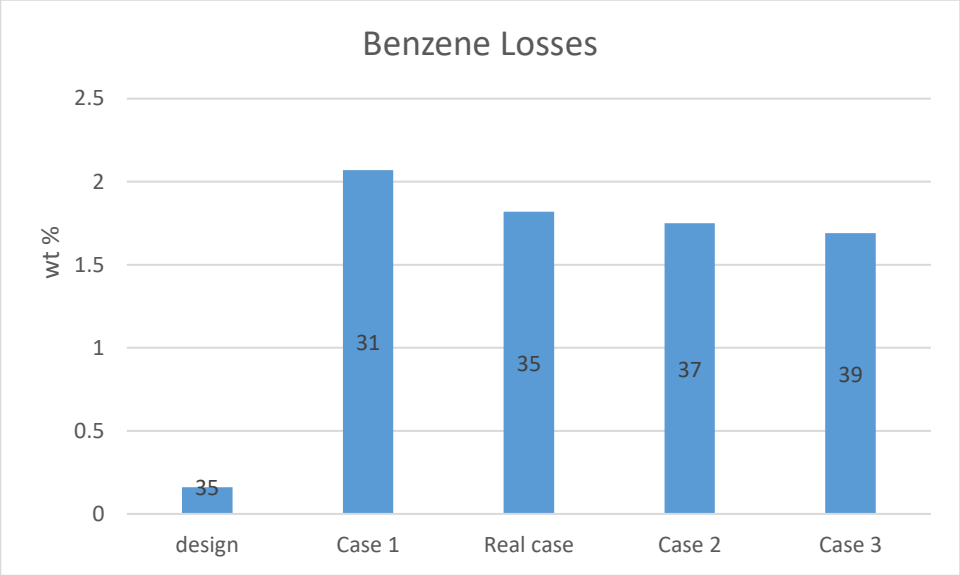


Figure IV.17: *The effect of the feed stage inlet on the benzene losses.*

We notice that the design case still exhibits the lowest losses. However, it is noteworthy that relocating the feed inlet to higher stages reduces benzene losses, offering some optimization for the real case with minimal changes to the top and bottom temperatures. Despite these improvements, the current modifications are not sufficient to come close to the range of the design case in terms of benzene losses. Therefore, we can neglect them as they do not provide significant impact.

IV.4.4.2. Lean Solvent Temperature Influence

We maintain the same operating parameters, and the only change we make is to the lean solvent temperature, which varies from 80 to 110°C. We increase the temperature and analyze the results The table below displays the results obtained from the simulation:

Table IV.9: *Results of optimizing the lean solvent temperature.*

Operating conditions	design	Case 1	Real case	Case 2	Case 3
Tº Top ˚C	89,1	90,6	90,68	90,69	90,75
Tº Bottom ˚C	165	161	162,30	163,70	163,90
Pº Top (kg/cm^2_g)	0,7	0,67	0,67	0,67	0,67
Reflux	0,34	0,14	0,14	0,14	0,14
%Benzene in the feed	32,36	21,04	21,04	21,04	21,04
Solvent/Feed ratio	1,66-2,5	1,3	1,3	1,3	1,3
Tº inlet solvent ˚C	100-110	80,00	88,4	96	110
Tº inlet feed ˚C	93,1	84,6	84,6	84,6	84,6
Benzene Losses %	0,07-0,16	1,92	1,82	1.73	1,63

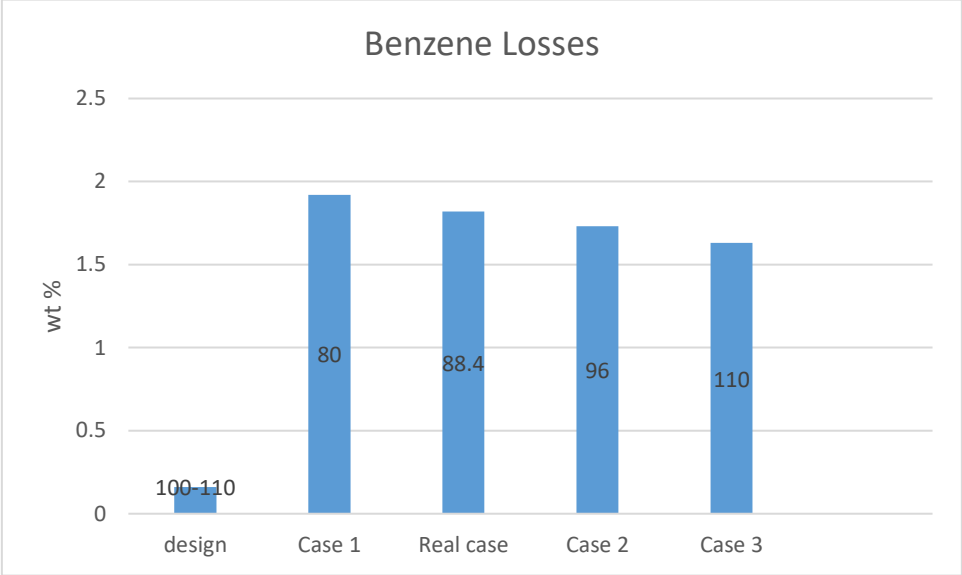


Figure IV.18: *The effect of the lean solvent temperature on the benzene losses.*

We observed that increasing the lean solvent temperature led to a notable reduction in benzene losses, indicating optimization in the real case. However, it is important to note that despite this improvement, the resulting benzene losses remained outside the desired range defined by the design specifications. Consequently, for practical considerations, we have chosen to disregard this influence.

IV.4.4.3. EDC Operating Pressure Influence

We simulate the column by maintaining the same operating parameters, with the only changes being applied to the operating pressure of the EDC system, targeting either the reboiler or condenser pressure. We increase the pressure subsequently conduct an analysis then we discuss the results.

The table below displays the results obtained from the simulation:

Table IV.10: *Results of optimizing the reboiler pressure*.

	Design	**Real case**	**Case 1**	**Case 2**
Reboiler pressure	1,27	1,27	2	2,5
Benzene losses %	0,16	1,82	1,70	1,52

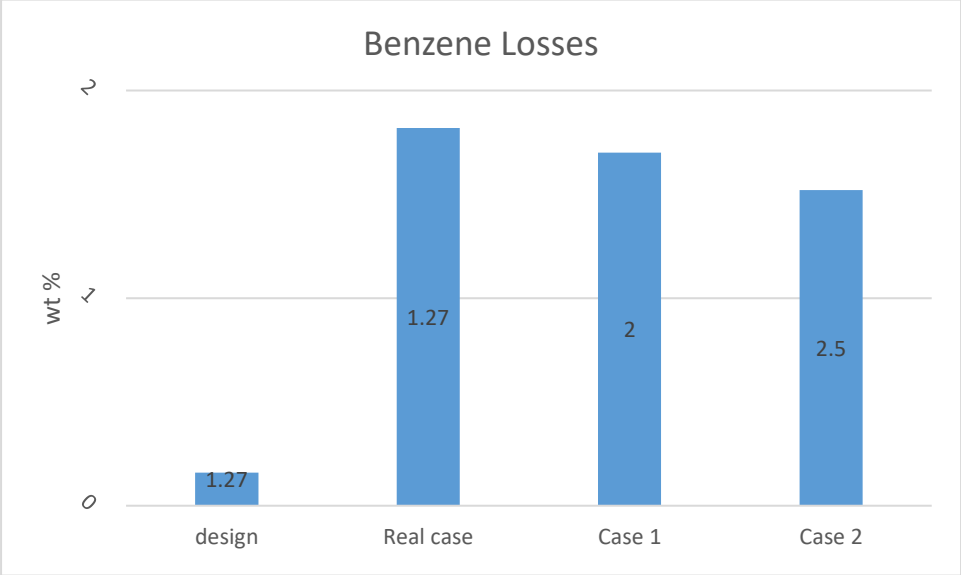


Figure IV.19: *The effect of the reboiler pressure on the benzene losses.*

We noticed a reduction in benzene losses when increasing the reboiler pressure, indicating optimization in the real case. However, despite this improvement, the achieved benzene losses remained significantly distant from the design specifications. Therefore, for practical considerations, we have chosen to neglect this influence.

IV.4.4.4. Solvent to Feed Ratio (S/F) Influence

We simulate the column and maintain the same operating parameters while solely applying modification to the solvent to feed ratio. Specifically, we increased the ratio to the optimum value recommended by the design. Subsequently, we conducted a comparison between the obtained cases and the design specifications.

The table below displays the results obtained from the simulation:

Table IV.11: *Results of optimizing the solvent to feed ratio.*

Operating conditions	design	Real case	Case 1	Case 2
Tº Top ˚C	89,1	90,68	90,86	90,77
Tº Bottom ˚C	165	162,30	164,40	168,20
Pº Top (kg/cm²_g)	0,7	0,67	0,67	0,67
Reflux	0,34	0,14	0,14	0,14
%Benzene in the feed	32,36	21,04	21,04	21,04
Solvent/Feed ratio	1,66-2,5	1,3	1,7	2,5
Tº inlet solvent ˚C	100-110	88,4	88,4	88,4
Tº inlet feed ˚C	93,1	84,6	84,6	84,6
Benzene Losses %	0,07-0,16	1,82	1,00	0.12

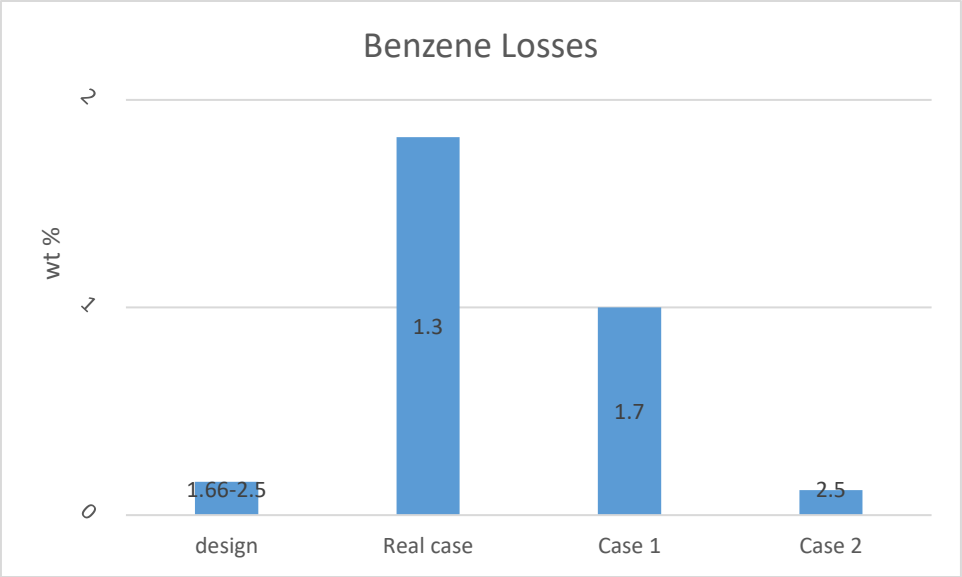


Figure IV.20: *The effect of the solvent to feed ratio on the benzene losses.*

We noticed that increasing the solvent to feed ratio resulted in a significant reduction of benzene losses. Furthermore, as the ratio was further increased, the losses continued to decrease. This change effectively optimized the real case and minimized the benzene losses within the design range. The solvent/feed ratio demonstrated its efficiency in achieving this outcome, indicating its potential for optimizing future cases.

Conclusion

Monitoring the operating parameters alone does not solve the issue of losses. Therefore, we conducted a simulation of C-51 in order to find the optimal operating parameters.

To minimize benzene losses, we have detected that the current operating parameters and feed quality deviate significantly from the design range, resulting in increased losses in the raffinate stream based on our results in HYSYS.

Therefore, it is necessary to bring the operating parameters closer to the design range as soon as possible to reduce these losses.

The influence of most variables can be neglected in our study since it was not significant and did not provide the desired numerical outcomes. However, an exception should be made for the feed to solvent ratio, as it was found to have a significant impact.

The most impactful change we can apply to improve benzene recovery is adjusting the solvent/feed ratio, it is necessary to operate at a high S/F ratio, the value should be close to or even greater than 2.5.

General Conclusion and Recommendations

General Conclusion

Our study was conducted during a practical internship carried out at the end of our academic program. This internship took place within the 200 unit at the Skikda refinery. This unit was designed for aromatics extraction. It utilizes the light reformate derived from Unit 100 (magnaforming), which involves the reformation of naptha 'B' to serve as an aromatic source for extraction.

Our study focuses on monitoring operational parameters from the start of the unit until the present day and conducting a simulation of the extractive distillation column (C-51), using the obtained results.

The monitoring allowed us to identify the parameters directly influencing benzene losses.

We used Aspen HYSYS V12.1 software as an investigation tool to simulate the process. It aims to find the appropriate thermodynamic model for both the unit's design case and the real case. This is done in order to determine the optimal operating conditions that will lead to a raffinate benzene content similar to that of the design. This method allowed us to:

- Verify and determine the steps and parameters of C-51 required for simulating both the current and design cases;
- Conduct a comparison between the real and design cases to provide further insights into the issue of benzene losses;
- Vary the operating parameters of the column to examine their influence on the loss of benzene;
- Determine the most influential parameters for optimizing the column and reducing benzene losses.

Through our study, we have achieved satisfactory and acceptable outcomes, enabling us to gain a comprehensive understanding of the column's behavior. We were able to effectively minimize benzene losses by utilizing various parameters. However, among these parameters, the Solvent/Feed ratio had the most significant impact. Optimizing the S/F ratio allowed us to successfully reduce benzene losses within the desired design range.

Recommendations

Based on the results of our study, we have several recommendations to enhance unit performance. These recommendations aim to optimize the operation and efficiency of the unit, leading to improved overall performance and product quality. By implementing these recommendations, we anticipate significant advancements in reducing benzene losses and achieving higher levels of aromatics purity. The following recommendations can be considered:

- Adjusting the solvent/feed ratio, it is necessary to operate at a high S/F ratio, the value should be close to or even greater than 2.5;
- Increasing the EDC operating pressure and this will Increase top and bottom temperature, resulting in enhanced benzene recovery;
- The higher the aromatics in feed, requires more stages below the feed tray. Therefore, we have to ensure that the feed location is adjusted accordingly;
- Increasing the lean solvent temperature will increase the solvent solvency, which reduces the solvent viscosity, thereby increasing mass transfer of aromatics and improving recovery;
- Operating the column based on the operating conditions provided by the manufacturer to achieve the desired results;
- actively adjusting and optimizing the process variables will enable us to enhance the efficiency of the extractive distillation process;
- The shutdown and cleaning procedure is critical. The unit staff must clean the column and perform maintenance whenever increased benzene losses are observed;
- For future studies, it is necessary to conduct simulations using Aspen Plus. This software provides a variety of column options with higher precision and more extensive features. The engineer should select the RadFrac column for the simulation. Additionally, ensuring the availability of solvent structure data is crucial for accurately simulating and optimizing the Extractive distillation column.

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Appendices

Appendix A: Presentation of Skikda Refinery

A.1. General Presentation of the Skikda Refinery

The Skikda oil refinery complex, called RA1/K, has the mission of transforming crude oil from Hassi Messaoud with a processing capacity (18 million t/year), as well as imported reduced crude oil (277,000 t/year).

A.1.1. Geographic Location

This refinery is located in the industrial area 7 km east of Skikda and 2 km from the sea, it is built on an area of 190 hectares with a current workforce of about 1280 workers. It is supplied with Algerian crude by crude from Hassi Messaoud.

The transport of crude oil is carried out using a pipeline at a distance from the oil fields to the complex of 760 km.

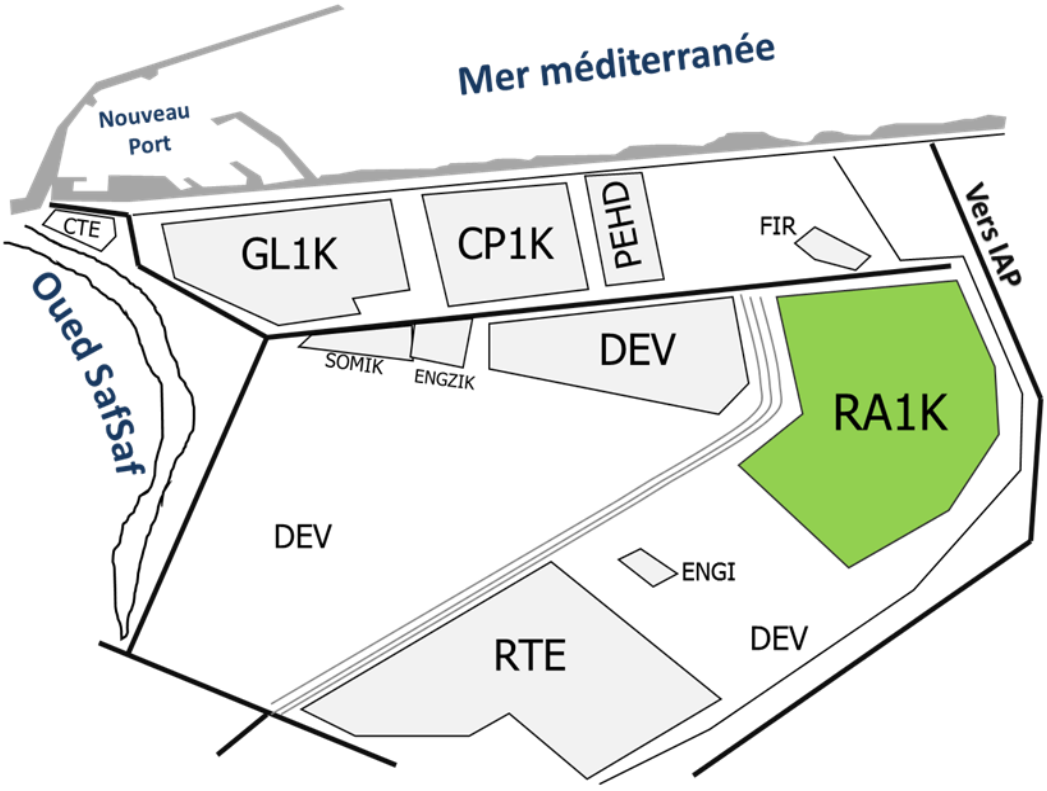


Figure A.1: *Geographical location of the Skikda refinery.*

A.1.2. Construction History

The refinery was built in January 1976 following a contract signed on April 30, 1974 between the Algerian government and the Italian manufacturer SNAM PROGETTI and SAIPEM.

The start of the construction site began on January 2, 1976, until March 1980, the progressive start of the production units followed one another as follows:

Table A.1: *Dates of the progressive start-up of production units at the Skikda refinery.*

Unit	Capacity (t/year)	Date
Topping (U10)	7,500,000	1980
Topping (U11)	7,500,000	1980
SepLPG ventilation (U30)	306,500	1980
SepLPG ventilation (U31)	283,000	1980
Catalytic reforming (U-100)	1,165,000	1980
Extraction and fractionation of aromatics (U200)	285,000	1980
Crystallization of para xylene (U400)	430,000	1980
Vacuum distillation and oxidation of bitumen (U70)	277,000	1980
Reforming Catalytic(U103)	1,165,000	1993
SepLPG ventilation (U104)	96,000	1993
Pstorage arch(U600)	2,700,000 (m3)	1980 and 1993
Thermoelectric plant	-	1980thsummer 1993

A.2. Presentation of the Deferent Production Unit

The refinery is equipped with the following facilities:

- ✓ Unit 10/11 : atmospheric distillation (TOPPING).
- ✓ Unit 100: pretreatment and catalytic reforming (MAGNAFORMING).
- ✓ Unit 101/103: pretreatment and catalytic reforming (PLATFORMING).
- ✓ Unit 30/31 and 104: gas treatment and separation (LPG).
- ✓ Unit 200 : extraction of aromatics.
- ✓ Unit 400: crystallization and separation of paraxylene.
- ✓ Unit 500: isomerization of m, ortho xylene to paraxylene.
- ✓ Unit 700/701/702/703: isomerization of light naphtha A.
- ✓ Unit 70: vacuum distillation (production of bitumen).

The utilities are :

- ✓ Unit 600: storage, mixing and shipping (MELEX).
- ✓ Unit 62 : water demineralization.
- ✓ Unit 1050: thermal electric power plant (CT E).
- ✓ Unit 900 : hydrogen purification.

A.2.1. Unit 10-11(Atmospheric Distillation)

Topping or atmospheric distillation aims to split the crude into different stabilized cuts that can be used to obtain finished products (naphtha, gas oil, jet). Units U10-11 process Hassi Messaoud crude for the following products: LPG, Iso-pentane, Naphtha A, Naphtha B (89.5°-155°), Naphtha C (155°-180°), Kerosene (180° -225°), Light Diesel (225°-320°), Heavy Diesel (320°-360°), and Residue (>360°).

A.2.2. Units 1000 and 103(Magnaforming, Platforming Units)

The purpose of Magnaforming and Platforming is to transform the medium and heavy naphtha obtained from Topping into reformate to be used as filler for aromatic units (units 200 and 400). This transformation results in an increase in the octane number from 45 to 99, thus making it possible to use the reformate obtained for the manufacture of gasoline.

A.2.3. Unit 30-31-104(Separation and Gas Treatment)

These units are intended to process the liquid gases coming from units 10, 11, 100 and 103 in the following order:

- **Unit 30**: treats the liquid gas which comes from unit 100, in particular those at the top of column C7 where the LPGs are separated from the pentane.
- **Unit 31**: receives gases from the top of the gasoline stabilization columns of the two Topping units.
- **Unit 104**: it was recently designed with the new Platforming unit 103 in order to process the GPLs coming from this unit.

A.2.4. Unit 200 (Extractions of Aromatics)

The aromatics extraction plant has been designed to extract aromatics from reformed gasoline which will then be fractionated into very pure benzene and toluene.

The feed consists of the light reformate cut coming directly or through a tank from the C5 splitter column of the reformate from unit 100.

A.2.5. Unit 400 (Separation of Paraxylene)

This unit is designed to recover para-xylene, a highly sought-after product on the market. The charge coming from the Magnaforming unit, makes it possible by crystallization to separate the para-xylene from the other xylenes (metha-ortho) and ethyl-benzene. Para-xylene is marketed as it is, the rest can be used as a base for obtaining gasolines or marketed in the form of a xylene mixture which can be used as a solvent for the manufacture of paints, etc.

A.2.6. Unit 500 (M-Xylene Isomerization)

The aromatics isomerization plant has been designed to recover the filtrate from the crystallizers of Unit 400 (p-xylene extraction unit) and the isomerism, after which the isomerate obtained will be separated into two essential fractions:

- A fraction rich in benzene sent to Unit 200.

- The other rich in p-xylene sent to Unit 400.

The main purpose of this unit is to increase p-xylene production.

A.2.7. Units 700/701/702/703 (Light Naphtha Isomerization Unit)

Their purpose is the conversion of normal paraffins into iso-paraffins is a reaction increasingly sought by the refiner to obtain a high-octane number without adding additives. Paraffins ranging from butane to hexane can be isomerized using modern, highly active platinum catalysts. Isomerization can be taken to extremes by the use of distillation and/or molecular sieve separation of unconverted normal paraffins.

The C5-C6 cuts can also be completely isomerized into highly sought-after high octane components for the gasoline pool.

The isomerization process has become a valuable tool for the refiner to broaden the range of its products and improve their qualities, while increasing the flexibility of operations and their profitability. In addition, the production of these high octane, but aromatic-free constituents reduces the contribution to the gasoline pool of the aromatic-rich reformate, thereby improving gasoline quality in terms of fuel protection. environment, which today is a very important factor.

In the Skikda refinery, two trains have been installed for the isomerization of the light fraction of the gasolines produced at the toppings (U10 & U11) in order to provide an aromatic-free additive to the pool of gasolines for the manufacture of fuels.

A.2.8. Unit 70 (Bitumen Production)

Unit 70 was designed to process 271,100 t/year of imported reduced crude oil (BRI) which can be:

- Load A: TIA residue juan medium 372°C plus.
- Charge B: heavy juan TIA residue 450°C plus.
- Charge C: Kuwait crude residue.

The unit mainly consists of a vacuum distillation column and a bitumen oxidation reactor. The column bottom product is ordinary road bitumen which is sent:

- A part towards storage.
- The other part as filler to the oxidation section where it will be oxidized by means of air into oxidized bitumen.

A.2.9. Unit 600 (MELEX Unit)

Mixing, loading and shipping, he takes care of:

- Storage bins for the different loads and products of the units.
- Shipping of products to the various storage depots, example: El-Kheroub depot.
- Mixing diesel fuels.
- Controls the loading of products which is at the port of Skikda.

A.2.10. Thermoelectric Plant

It is the nervous system of the refinery, The CTE consists of 11 sections namely:

- Section 62: for the production of demineralised water.
- Section 1020: for water cooling towers.
- Section 1030: for the storage and pumping of dam water or drinking water.
- section 1040: for the storage and pumping of fire-fighting water.
- Section 1050: for the generation of “boiler” steam.
- Section 1060: for the recovery and treatment of condensate.
- Section 1070: or Fuel-Gas system.
- section 1080: for the production of instrument air and service air.
- Section 1100 for effluent treatment.
- Section 1110: production of nitrogen (N_2).
- Electricity production section.

A.2.11. Unit 900 (Hydrogen Purification Unit)

Its purpose is to increase the purity of the hydrogen from unit 100, in order to send it to the other hydrogen-consuming units (unit 500, etc.).

A.3. Rehabilitation and Adaptation Projects of the Skikda Refinery

A.3.1. Rehabilitation Plan and Program

Table A.2: *Rehabilitation plan for RA1K units.*

No.	Units	Designation	Front capacity Rehabilitation (kg/h)	Capacity after Rehabilitation (kg/h)
1	Topping-1 (*)	10	7,500,000	9,375,000
2	Topping-2 (*)	11	7,500,000	9,375,000
3	GasPlant-1 (*)	30	306,500	339,500
4	GasPlant-2 (*)	31	283,000	339,500
5	GasPlant-3	104	96,000	Instrument revamp @
6	PNaphtha reprocessing	100	1,165,000	Instrument revamp @
7	Reform I (*)	100	1,165,000	1,174,600
8	DrySplitter Platformat (**)	100	-	989 950
9	PNaphtha reprocessing	101-103	1,165,000	Instrument revamp @
10	Extraction of aromatics (*)	200	285,000	627 100
11	Extraction of Paraxylene (#)	400	430,000	1,782,800
12	IXylene somerization (**)	500	-	1,380,400
13	Hydrogènes urificatione(**)	900	-	27,200
14	Sacid water tripper II (*)	10	33,530	28,000
15	Strip acidic waters I (**)	12	-	17,070
16	Bitumen blowing unit	70	277,000	Instrument revamp @
17	Kerosene processing unit No. 1	20	750,000	Instrument revamp @
18	Kerosene processing unit No. 2	21	750,000	Instrument revamp @

(*) = renovated; (**) = New; (#) = moved and renovated; @=including HAZOP

A.3.2. Production Report of the RA1K Refinery

In the Table A.3. Below illustrates the production balance of the RA1K before and after its rehabilitation.

Table A.3: *Production report of the RA1K before and after the rehabilitation*.

Charges	Avant Réhabilitation	Apres Réhabilitation
Pétrole brut, TPA	15 000 000	18 000 000
Produits		
GPL	365 000	644 200
Naphta	1700 000	3 753 800
Essence	2 180 000	2 135 400
Jet a1	1 500 000	1 500 000
Diesel	4 250 000	5 913 800
Fuel oil	4 300 000	4 270 800
Benzène	90 000	197 300
Toluène	11 000	16 900
Paraxylène	38 000	22 0100

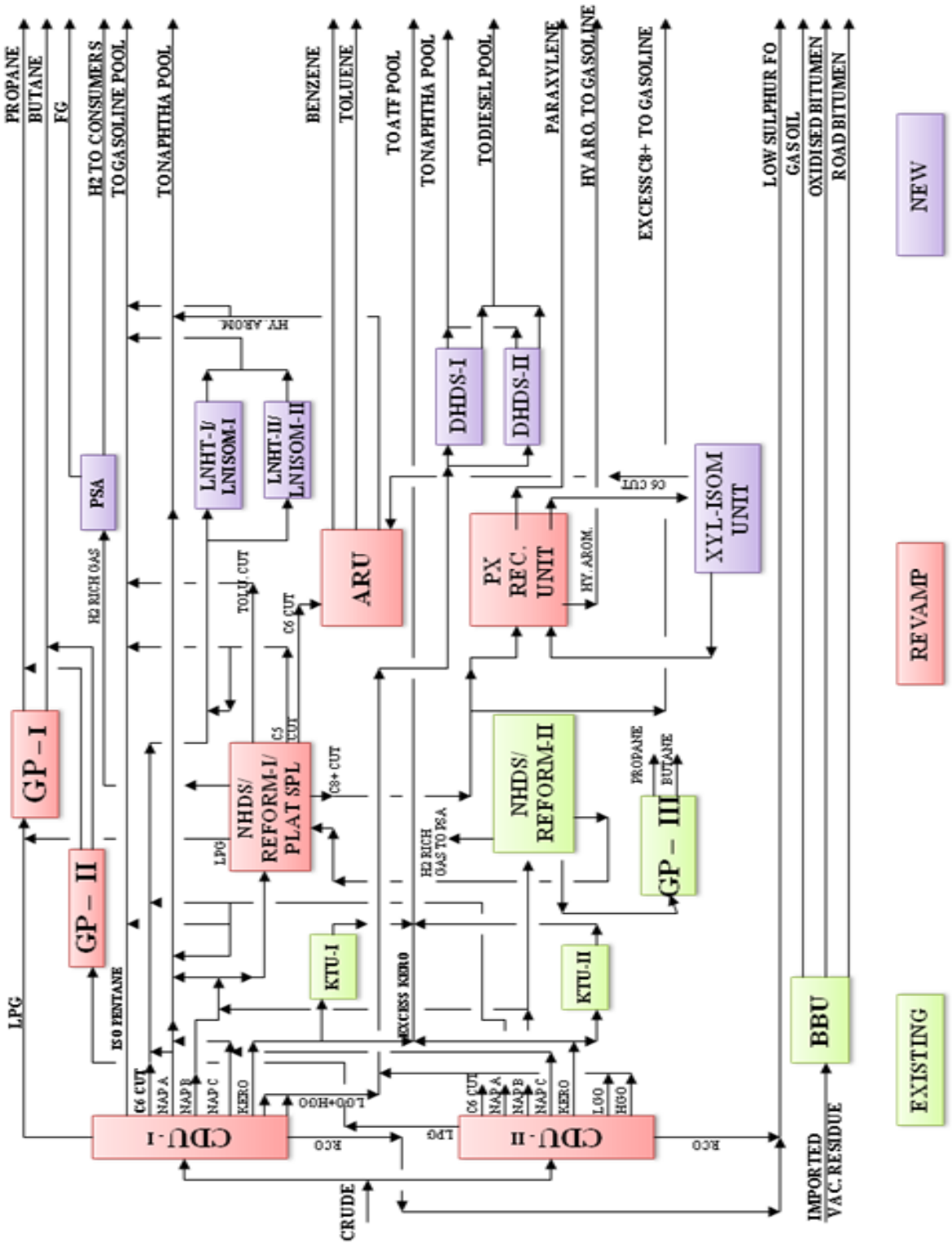
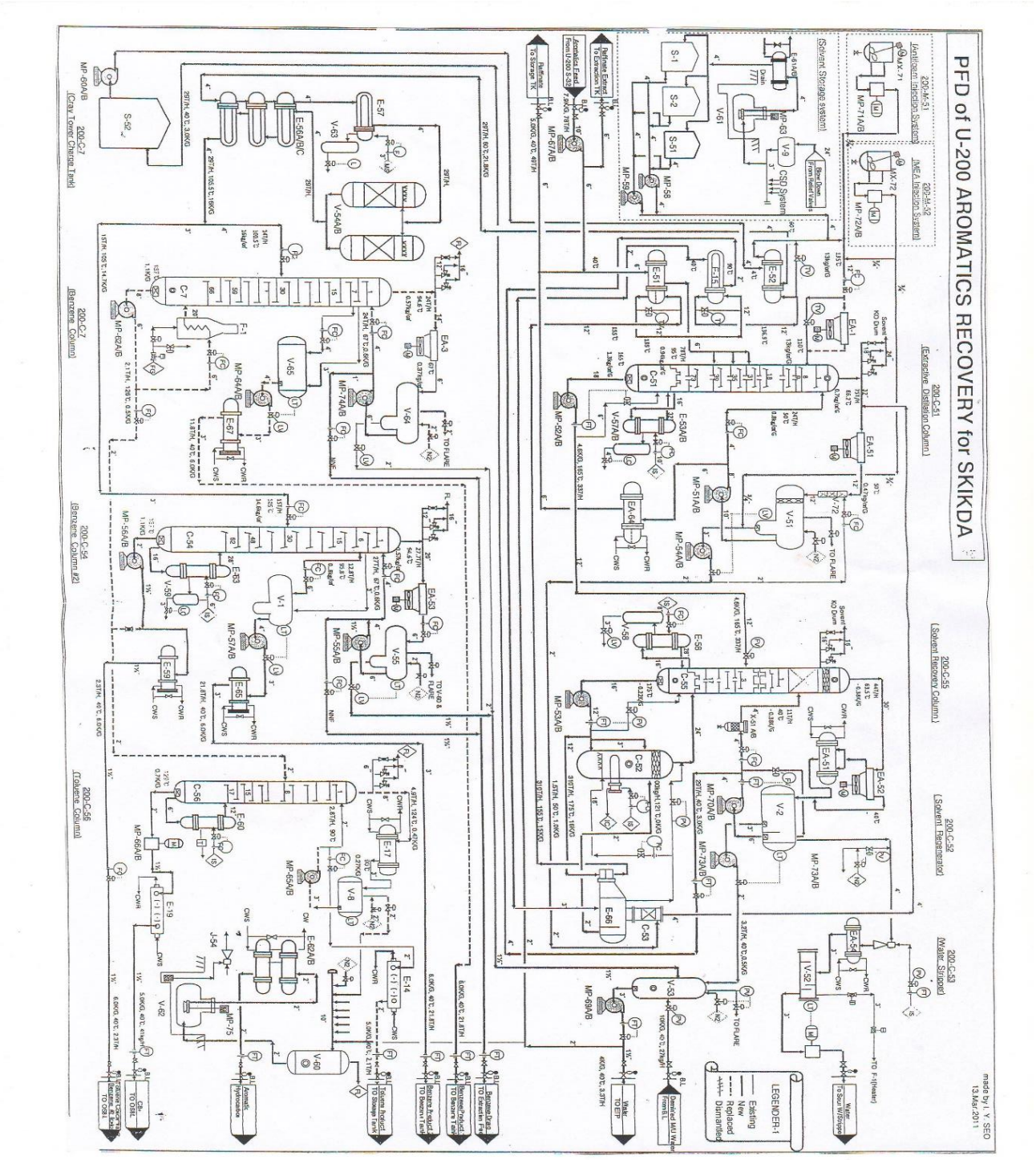


Figure A.2: Diagram of the main processes in Skikda refinery.

Appendix B: Process Flow Diagram of Aromatics Recovery Unit-200\



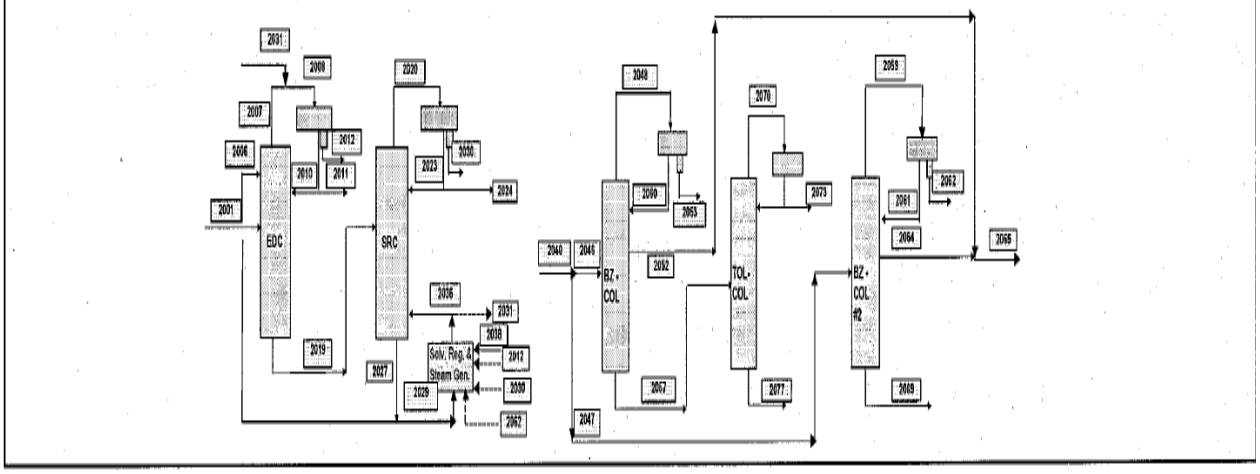
Appendix C: Materials Balance

AROMATICS EXTRACTION SECTION

	FEED								PRODUCT								PRODUCT											
Stream Number	2001RE		2005RE		2007RE		2008RE		2010RE		2011RE		2012RE		2019RE		2020RE		2023RE		2024RE		2027RE		2029RE		2030RE		2031RE		2036RE		2034RE	
Stream Description	Feed to Extn.		Lean Solvent to EDC		EDC Ovhd vapor		EDC Vapor Cond.		EDC Reflux		Raffinate to Stg BL		EDC wtr to wtr strip		EDC Bottoms to SRC		SRC ovhd vapor		SRC Reflux		Extract to Storage		SRC Btms		Ln Solv to Reg		SRC wtr to Stg Drum		Water strp ovhd		Strip Steam to SRC		Make-up Water	
Stream Phase	Liquid		Liquid		Vapor		Liquid		Liquid		Liquid		Liquid		Mixed		Vapor		Liquid		Liquid		Liquid		Liquid		Liquid		Vapor		Vapor		Liquid	
Total Mass Rate, Kg/Hr	74251		297022		70217		70317		22715		46119		1484		323751		42389		10956		28173		298802		1800		3259		100		6464		27	
Composition	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr
C4 Paraffins	0.06	41.4	0.00	0.0	0.09	61.8	0.09	61.7	0.09	20.4	0.06	41.4	0.00	0.0	0.09	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C5 Paraffins	1.68	1244.7	0.00	0.0	2.65	1857.7	2.64	1857.7	2.70	613.1	2.70	1244.7	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C6 Paraffins	32.56	24174.8	0.00	0.0	51.39	36081.8	51.31	36081.9	52.42	11907.0	52.42	24174.9	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.01	0.0	0.00	0.0	0.00	0.0
C7 Paraffins	22.99	17067.9	0.00	0.0	36.28	25474.5	36.23	25474.4	37.01	8406.6	37.01	17067.9	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C8 Paraffins	0.08	62.7	0.00	0.0	0.13	93.6	0.13	92.9	0.14	30.9	0.14	62.7	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C9 Paraffins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C5 Olefins	0.00	0.3	0.00	0.0	0.00	0.4	0.00	0.4	0.00	0.1	0.00	0.3	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C6 Olefins	0.93	692.7	0.00	0.0	1.47	1033.1	1.47	1033.0	1.50	340.9	1.50	692.7	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C7 Olefins	0.53	395.5	0.00	0.0	0.84	590.3	0.84	590.4	0.86	194.8	0.86	395.5	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C8 Olefins	0.00	0.5	0.00	0.0	0.00	0.7	0.00	0.7	0.00	0.2	0.00	0.5	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C5/C6 Naphtl. (CP+MCP)	1.67	1242.6	0.00	0.0	2.64	1854.6	2.64	1854.6	2.69	612.0	2.69	1242.6	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.01	0.0	0.00	0.0	0.00	0.0
C6 Naphthenes (CH)	0.68	505.9	0.00	0.0	1.08	758.0	1.07	755.1	1.10	249.2	1.10	505.9	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C7 Naphthenes	0.78	580.3	0.00	0.0	1.23	866.2	1.23	866.2	1.26	285.8	1.26	580.4	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C8 Naphthenes	0.03	22.4	0.00	0.0	0.05	31.9	0.05	31.9	0.05	10.5	0.05	21.4	0.00	0.0	0.00	1.0	0.00	1.4	0.00	0.4	0.00	1.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
Benzene	32.36	24029.1	0.00	0.7	0.15	103.4	0.16	110.5	0.16	30.4	0.16	74.0	0.00	0.0	7.40	23963.1	76.51	32277.9	85.03	9315.9	85.03	23955.1	0.00	0.9	0.00	0.0	0.22	7.0	7.02	7.0	0.00	0.0	0.00	0.0
Toluene	5.64	4189.2	0.00	0.3	0.00	0.1	0.00	0.3	0.00	0.1	0.00	0.2	0.00	0.0	1.29	4189.7	13.73	5818.3	14.87	1629.1	14.87	4189.0	0.00	0.3	0.00	0.0	0.01	0.2	0.18	0.2	0.00	0.0	0.00	0.0
C8 Aromatics	0.00	1.2	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	1.2	0.00	1.8	0.00	0.5	0.00	1.2	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
Tochlv+100	0.00	0.0	99.21	294656.5	0.00	0.3	0.00	0.3	0.00	0.1	0.00	0.2	0.00	0.0	91.01	294656.6	0.00	0.0	0.00	0.0	0.00	0.0	99.21	296442.0	99.21	1785.8	0.00	0.0	0.00	0.0	27.54	1785.8	0.00	0.0
Water	0.00	0.0	0.79	2344.2	2.01	1411.8	2.14	1504.7	0.03	6.8	0.03	13.8	100.00	1484.0	0.29	939.0	7.70	3269.4	0.10	10.4	0.10	26.8	0.79	2359.0	0.79	14.2	99.78	3252.2	92.77	92.8	72.46	4698.3	100.00	27.0
TOTAL	100.0	74251	100.0	297022	100.0	70217	100.0	70317	100.0	22715	100.0	46119	100.0	1484	100.0	323751	100.0	42389	100.0	10956	100.0	28173	100.0	298802	100.0	1800	100.0	3259	100.0	100	100.0	6464	100.0	27

POST FRACTIONATION SECTION

	FEED																						PRODUCT						PRODUCT			
Stream Number	2040RE		2046RE		2047RE		2048RE		2050RE		2052RE		2053RE		2057RE		2059RE		2061RE		2062RE		2064RE		2065RE		2065RE		2070RE		2073RE		2077RE	
Stream Description	Extract from Storage		Feed to Bz Col		Feed to Bz col #2		Bz col ovhd vapor		Bz col reflux		Benzene product		Bz Column Water		Tol Col Feed		Bz col #2 ovhd vapor		Bz col #2 reflux		Bz Column Water		Benzene product #2		Bz pdt to Stg BL		Tol. Conc. to BL		Tol Col Ovhd vap		Tol pdt to Stg BL		Tol Btms to Stg BL	
Stream Phase	Liquid		Mixed		Mixed		Vapor		Liquid		Liquid		Water		Mixed		Vapor		Liquid		Water		Liquid		Liquid		Liquid		Vapor		Liquid		Liquid	
Total Mass Rate, Kg/Hr	26173		14000		14173		24428		24412		11906		13		2081		25928		25914		13		12061		23957		2107		4805		2040		41	
Composition	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr	wt %	Kg/hr
C4 Paraffins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C5 Paraffins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C6 Paraffins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C7 Paraffins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C8 Paraffins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C9 Paraffins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C5 Olefins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C6 Olefins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C7 Olefins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C8 Olefins	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C5/C6 Naphtl. (CP+MCP)	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C6 Naphthenes (CH)	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C7 Naphthenes	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
C8 Naphthenes	0.00	1.0	0.00	0.5	0.00	0.5	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.02	0.5	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.02	0.5	0.01	0.5	0.01	0.2	0.64	0.3
Benzene	85.03	23955.1	85.03	11903.9	85.03	12051.2	99.67	24345.8	99.72	24344.8	99.98	11903.6	0.03	0.0	0.00	0.1	99.67	25843.0	99.72	25842.0	0.00	0.0	99.99	12049.8	99.99	23953.4	0.00	0.1	0.01	0.2	0.01	0.1	0.00	0.0
Toluene	14.87	4189.0	14.87	2081.6	14.87	2107.4	0.00	0.1	0.00	0.1	0.02	1.8	0.00	0.0	99.94	2079.9	0.00	0.1	0.00	0.1	0.00	0.0	0.01	1.2	0.01	3.0	99.94	2106.2	99.98	4803.6	99.98	2039.9	98.07	40.0
C8 Aromatics	0.00	1.2	0.00	0.6	0.00	0.6	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.03	0.6	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.03	0.6	0.00	0.1	0.00	0.1	1.29	0.5
Tochlv+100	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
Water	0.10	26.8	0.10	13.3	0.10	13.5	0.33	80.3	0.29	67.2	0.00	0.2	100.00	13.1	0.00	0.0	0.33	84.7	0.28	71.4	100.00	13.3	0.00	0.2	0.00	0.4	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
TOTAL	100.0	26173	100.0	14000	100.0	14173	100.0	24426	100.0	24412	100.0	11906	100.0	13	100.0	2081	100.0	25928	100.0	25914	100.0	13	100.0	12061	100.0	23957	100.0	2107	100.0	4805	100.0	2040	100.0	41



Appendix D: Stream Summary

Stream Number		2001RE	2002RE	2007RE	2008RE	2009RE	2010RE	2011RE	2012RE	2013RE	2014RE	2015RE	2016RE	2018RE	2002RE	2003RE	2004RE	2005RE	2006RE	2021RE	2033RE	2034RE	2040RE	2041RE
Stream Description		Preheated Feed to EDC	Preheated Feed to EDC	EDC Overhead vapor	EDC Vapor Condens	EDC Overhead Liq to Receiver	EDC Reflux	Raffinate to Storage	EDC Water to water strip	EDC Water to Mixer	EDC Steam Rate In	EDC Steam Rate Out	EDC Bottoms	EDC Bottoms to SRC	Lean Solv to Feed Preheater	Lean Solv to Water Preheater	Lean Solv to Ext Preheater	Lean Solv to Cooler	Lean Solvent to EDC	Water strip overhead	Water to Preheater	Water from Preheater	Extract from Clay Tower Chg Pump	Frac Feed to FeEff Exch
Stream Phase		Liquid	Mixed	Vapor	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Mixed	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Vapor	Liquid	Liquid	Liquid	Liquid
Temperature	C	40.0	93.1	88.2	50.0	50.0	50.0	40.0	50.0	50.0	120.2	165.0	166.0	165.1	154.3	137.5	138.3	134.5	110.0	119.8	40.0	90.0	40.0	50.0
Pressure	kg/cm2g	4.97	0.94	0.67	0.47	0.42	0.80	5.00	1.00	0.50	1.25	1.27	1.27	4.40	15.10	14.40	13.70	13.00	0.89	0.97	4.20	2.70	22.50	21.80
Mole Flow	kg-mol/hr	861.6	861.6	838.7	843.9	1143.6	251.3	510.2	62.4	299.7	3771.7	3771.7	2856.5	2856.5	2592.2	2592.2	2592.2	2592.2	2592.2	5.2	182.9	182.9	353.6	353.6
Weight Flow	kg/hr	74251	74251	70218	70318	75718	22715	46116	1404	5400	383537	383537	323751	323751	297003	297003	297003	297003	297003	100	3300	3300	28173	28173
Total Sp. Enthalpy	kcal/kg	19.50	47.90	132.46	25.17	28.86	24.87	19.35	48.82	48.82	46.55	81.76	82.49	82.51	57.06	49.96	49.47	48.72	38.77	610.32	40.23	84.47	16.95	24.90
Enthalpy	x 1045 Kcal/hr	1.45	3.56	9.30	1.77	2.03	0.56	0.89	0.07	0.26	17.47	31.37	26.23	26.24	16.95	14.84	14.69	14.47	11.52	0.06	0.13	0.28	0.48	0.70
Molecular Weight		86.18	86.18	83.73	83.33	66.21	90.39	90.39	18.02	18.02	101.72	101.72	113.34	113.34	115.02	115.02	115.02	115.02	115.02	18.08	18.05	18.05	79.67	79.67
Vapor Pressure	kg/cm2	0.37	1.98	5.78	0.69	0.69	0.86	0.47	0.69	0.69	2.28	5.80	2.30	2.30	0.59	0.43	0.42	0.40	0.22	912.51	0.30	1.24	0.30	0.59
Critical Pressure	kg/cm2	38.02	38.02	48.58	49.65	66.76	30.53	30.53	225.56	225.56	61.41	61.41	52.19	52.19	57.85	57.85	57.85	57.85	57.85	222.46	225.47	225.47	49.89	49.89
True Critical T	C	280.8	280.8	251.2	251.9	284.0	238.7	238.7	374.2	374.2	470.5	470.5	520.8	520.8	547.4	547.4	547.4	547.4	547.4	372.7	374.2	374.2	293.8	293.8
Vapor Phase																								
Volume Flow (Std)	m3/hr		280.72	18797.52								20506.76								117.49				
Volume Flow (Flwg)	m3/hr		185.53	1514.82								14765.78								96.07				
Mole Flow	kg-mol/hr		12.5	838.7								914.9								5.2				
Weight Flow	kg/hr		1080	70218								58866								100				
Vapor Sp. Enthalpy	kcal/kg		126.89	132.46								165.89								610.32				
Specific Heat	kcal/kg-C		0.42	0.42								0.30								0.45				
Molecular Weight			84.83	83.73								65.43								18.08				
Density (Std)	KG/M3		3.78	3.74								2.92								0.85				
Density (Flwg)	KG/M3		5.71	4.65								4.05								1.16				
Viscosity	CP		0.01	0.01								0.01								0.01				
Conductivity	kcal/hr-m-C		0.02	0.02								0.02								0.02				
Compressibility			0.94	1.00								1.00								0.99				
CP/CV Ratio			1.07	1.06								1.11								1.22				
Liquid Phase																								
Volume Flow (Std)	m3/hr	100.45	98.98		103.80	109.21	33.76	68.55	1.49	5.41	332.33	265.50	265.47	265.47	234.96	234.96	234.96	234.96	234.96		3.31	3.31	31.94	31.94
Volume Flow (Flwg)	m3/hr	103.37	102.94		108.71	114.28	35.18	70.85	1.53	5.57	359.89	265.61	295.58	295.66	268.13	265.06	264.86	264.95	250.27		3.38	3.54	32.72	33.47
Mole Flow	kg-mol/hr	861.6	849.1		843.9	1143.6	251.3	510.2	62.4	299.7	3771.7	2856.5	2856.5	2856.5	2592.2	2592.2	2592.2	2592.2	2592.2		182.9	182.9	353.6	353.6
Weight Flow	kg/hr	74251	73191		70318	75718	22715	46116	1404	5400	383837	323772	323751	323751	297003	297003	297003	297003	297003		3300	3300	28173	28173
Molecular Weight		86.18	86.20		83.33	66.21	90.39	90.39	18.02	18.02	101.72	113.33	113.34	113.34	115.02	115.02	115.02	115.02	115.02		18.05	18.05	79.67	79.67
Liquid Sp. Enthalpy	kcal/kg	19.50	46.77		25.17	28.86	24.87	19.35	48.82	48.82	46.55	62.49	62.46	62.51	57.06	49.96	49.47	48.72	38.77		40.23	84.47	16.95	24.90
Specific Heat	kcal/kg-C	0.48	0.55		0.56	0.58	0.55	0.54	0.87	0.87	0.43	0.44	0.44	0.44	0.43	0.42	0.42	0.41	0.40		0.86	0.91	0.39	0.41
UOP K factor		11.58	11.57		12.58	12.22	12.57	12.57	8.76	8.76	8.22	8.07	8.07	8.07	7.91	7.91	7.91	7.91	7.91		8.76	8.76	9.78	9.78
Density (Flwg)	kg/m3	718.3	695.8		646.8	662.5	646.7	652.8	968.9	968.9	1066.0	1095.3	1095.3	1095.4	1150.6	1164.4	1165.3	1166.6	1186.7		977.3	933.0	851.0	841.7
Density (Std)	kg/m3	739.2	738.4		677.4	693.3	672.8	672.8	998.6	998.6	1154.4	1219.5	1219.5	1219.5	1264.1	1264.1	1264.1	1264.1	1264.1		998.3	998.3	882.1	882.1
Surface Tension,	dyne/cm	20.52	14.73		20.63	33.07	15.50	16.51	68.07	68.07	26.83	23.47	23.47	23.47	26.54	28.05	28.15	28.31	30.44		68.57	61.17	25.61	24.08
Conductivity	kcal/hr-m-C	0.10	0.09		0.09	0.10	0.09	0.09	0.56	0.56	0.12	0.11	0.11	0.11	0.12	0.12	0.12	0.12	0.13		0.53	0.56	0.12	0.11
Viscosity	CP	0.36	0.21		0.28	0.34	0.25	0.28	0.54	0.54	1.10	1.02	1.02	1.02	1.30	1.53	1.55	1.58	2.10		0.65	0.91	0.49	0.39

Appendix E: Physical and Chemical Properties of Techtiv_100^{sm}

9. Physical and chemical properties

Appearance

Form : liquid
Colour : yellowish
Odour : characteristic

Data relevant to safety

Changes in physical state

Melting temperature	9 °C
Boiling temperature	282 - 288 °C
Flash point	177 °C (Pensky Martens Closed Cup)
Ignition temperature	not determined
Self-ignition temperature	not determined
Lower explosion limit	not determined
Upper explosion limit	not determined
Vapour pressure	19.4 hPa at 150 °C
Density	1.26 g/cm3 at 20 °C
Relative vapour density (related to air)	not determined
Solubility in water	miscible
pH-Value	not determined
n-Octanol/water partition coefficient	log Pow 0.77 at 25 °C
Viscosity (dynamic)	10 mPa.s at 30 °C
Further information	None