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Optimization of light hydrocarbons recovery from the Magnaforming stabilizer (100-C-4) bottom product of U100, RA1K using Aspen HYSYS

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“Optimization of light hydrocarbons recovery from the Magnaforming stabilizer (100-C-4) bottom product of U100, RA1K using Aspen HYSYS”

Abstract

This work presents the simulation and optimization of the stripping system of Magnaforming unit (U100) at Skikda’s Refinery 1, with the aim of minimizing the light hydrocarbon fraction in the treated naphtha produced from catalytic reforming. This study will explore analytical methods for characterizing petroleum products, including ASTM D86 distillation and ASTM D6729 gas chromatography, as well as numerical methods for characterizing petroleum mixtures and modeling the unit operation used (distillation). The simulations and the results were generated using ASPEN HYSYS software based on design data and the optimization was carried out using the real plant operating conditions and composition.

Key words: Simulation, petroleum fluid characterization, Stripping systems, Aspen Hysys, process optimization.

“Optimisation de la récupération des hydrocarbures légers dans le produit de fond de la colonne stabilisatrice (100-C-4) de l’unité Magnaforming U100, RA1K à l’aide de Aspen HYSYS ”

Le présent projet représente la simulation et l’optimisation du système de stabilisation de l’unité Magnaforming (U100) de la raffinerie de Skikda 1, et qui a pour objectif de minimiser la fraction des hydrocarbures légers contenue dans le naphta traité issue du reformage catalytique. Cette étude va explorer les méthodes analytiques de caractérisation des produits pétroliers, notamment la distillation ASTM D86 et la chromatographie en phase gazeuse ASTM D6729 ainsi que la méthode numérique de caractérisation des produits pétroliers et la modélisation de l’opération unitaire ‘Distillation’. Les simulations et les résultats ont été généré à l’aide du logiciel Aspen HYSYS en se basant sur les données du cas design et l’optimisation a été réalisé en exploitant les conditions opératoires et les compositions dans cas réel.

Mots clés : Simulation, caractérisation des fluides pétroliers, systèmes de stripping, Aspen HYSYS, optimisation des procédés.

"تحسين عملية إزالة الهيدروكربونات الخفيفة من نواتج قاع عمود التجريد (100-ع-4) لوحدة التحسين التحفيزي (و100) لمركب تكرير البترول سكيكدة 1 باستعمال برنامج أسبن هايسيس"

هذه الدراسة عبارة عن تحسين بواسطة محاكاة لنظام التجريد التابع لوحدة الإصلاح التحفيزي (و100) بمركب تكرير البترول سكيكدة 1 الغرض من المشروع هو تقليل نسبة الغازات الخفيفة الموجودة في النافتا المعالجة بعملية الإصلاح التحفيزي.

ASTM D86 الدراسة ستطرح طرق تحليلية لتحديد خصائص المشتقات البترولية على غرار عملية التقطير

كما تشمل أيضا عملية رقمية لتحديد خصائص المشتقات ASTM D6729و عملية التحليل بالكروماتوغرافيا في الحالة الغازية البترولية و نمذجة عملية التقطير.

المحاكاة والنتائج تم توليدها باستعمال برنامج أسبن هايسيس استنادا على المعطيات في حالة التصميم و التحسين تم إنجازه بالاعتماد على ظروف التشغيل والتركيبات في الحالة الحقيقية.

الكلمات المفتاحية محاكاة تحديد خصائص المواد البترولية نظم التجريد أسبن هايسيس تحسين العمليات

REMERCIEMENT

Table of contents

List of tables

List of figures

General introduction

Gasoline, derived from the atmospheric distillation of petrol, is one of the world's most widely consumed fuels. The processing involved in gasoline production varies depending on the crude cut used. Light cuts, called naphtha, undergo catalytic reforming to convert low-octane naphtha into high-octane naphtha through reactions that transform linear paraffins into aromatic compounds or branched-chain hydrocarbons[1]. Heavy raw fractions are often subjected to catalytic cracking, a process that splits the large molecules into smaller ones, better suited to use as fuel oil[2].

Algeria ranks third in Africa (after Egypt and South Africa) and 36th globally in gasoline consumption[3], with an estimated 3.3 million tons consumed in 2023. Since 2021, Algeria has met its entire domestic gasoline demand[4], and the Skikda 1 refinery remains the largest gasoline producer among Algeria's five refineries, with a crude oil processing capacity of 16.5 million tons per year[5].

Gasoline is a flammable and volatile liquid composed of a mixture of hydrocarbons, primarily paraffins, naphthenes, and aromatics[6]. This fluid is used in spark-ignition engines. For this purpose, the fuel must meet a crucial requirement: resistance to autoignition. This phenomenon is linked to an index that allows us to control it, called the octane number. The higher the octane number, the more resistant the fuel is to autoignition. The minimum authorized octane number value in a country is the result of collaboration between various stakeholders, including governments, standardization bodies, and the oil industry. In Algeria, the minimum authorized value is 92, in Europe the 95 octane is the minimum authorized rate, and in America, its value must be between 91 and 92[7].

This project focused on the optimization of the stripping system of the U100 catalytic reforming unit of the Skikda 1 refinery. This system represents a critical step in maintaining the quality of the final product, gasoline, as it is the first step in the process of improving the products resulting from the catalytic reforming operation in the fractionation section of the unit. Optimization of this section was necessary due to a significant decrease in the octane number of the gasoline produced in unit 100.

This study will explore analytical methods for characterizing petroleum products, including ASTM D86 distillation and ASTM D6729 gas chromatography, as well as numerical methods for characterizing petroleum mixtures and modeling the operation of the unit used (distillation) by simulation using Aspen HYSYS.

Chapter 1: Presentation of the Magnaforming unit (U100) in Skikda refinery (RA1K)

1.1 Presentation of the RA1K:

The SKIKDA oil refinery, called RA1K is the largest refinery in Algeria, located in the industrial zone 7 kilometers east of Skikda and 2 kilometers from the sea. It covers an area of 190 hectares. The refinery is fed by Algerian petroleum crude from Hassi Messaoud, transported via a pipeline covering a distance of 760 kilometers from the oil field to the complex.
The refinery was constructed following a contract signed on April 30, 1974, between the Algerian government and the Italian companies SNAM PROGETTI and SAIPEM. Construction began on January 2, 1976, and was completed in March 1980. In 2013, the refinery underwent rehabilitation, including the installation of new units, renovation and capacity enhancement of some existing units, such as the U100 Magnaforming and Platforming unit. The rehabilitation and adaptation project were carried out by the South Korean company Samsung Engineering and Construction.
Currently, the Skikda refinery has a crude oil processing capacity of 18 million tons per year, along with imported reduced crude oil (300,000 tons per year)[8].

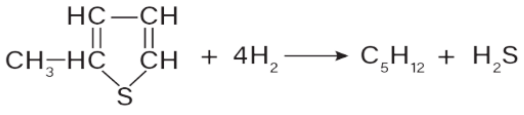
1.2 Presentation of the Magnaforming unit (U100)

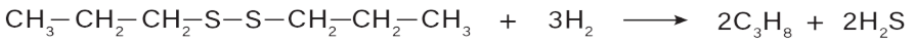
The Magnaforming unit (U100) operated by the Skikda refinery is based on the catalytic reforming process, which was originally developed to upgrade low-octane straight-run naphtha produced from Algerian crude oil by atmospheric distillation in unit 10 and unit 11, to high-octane fuels. The CR produces high-octane liquid rich in aromatic compounds with 6 to 10 carbon atoms, the highest proportions being limited to 7, 8 or 9. Chemical-grade hydrogen, light gas and liquefied petroleum gas (LPG) are also by-products of the reaction.
This unit could be divided into three sections as follows:

1.2.1 Hydrotreatment section

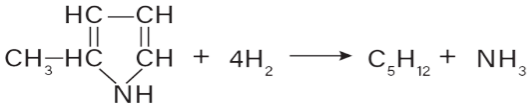
The aim of this section is to remove impurities present in various petroleum fractions, including nitrogen, oxygen, sulfur and metals. These impurities act as temporary or permanent poisons for the Magnaforming catalyst. In addition, they adversely affect the quality of the end products through pollution and corrosion problems. Feedstock processing takes place in a reactor called a hydrotreating reactor, where the metals are chemically absorbed by the catalyst. However, nitrogen, oxygen and sulfur are removed by the following chemical reactions[2]:

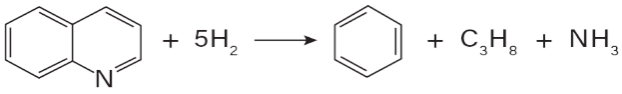
- **Desulfurization**



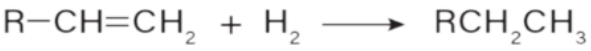


- **Denitrification**

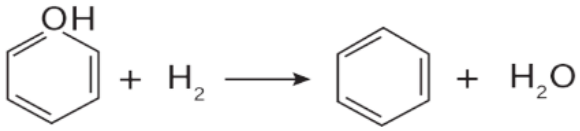




- **Hydrocarbon saturation**



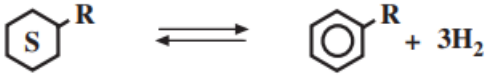
- **Oxygen removal**



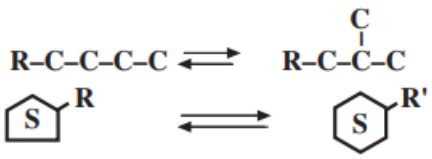
1.2.2 Reaction Section

The reaction section of the U100 is a semi-regenerative fixed-bed catalytic reforming process using 4 reactor beds operating with a rising temperature profile at the reactor inlet ranging from 448°C to 500°C and an operating pressure varying between 14.5 Kg/cm² and 9.24 Kg/cm². The heat required for the reactions is supplied by four heaters. Numerous reactions take place during reforming processes, these reactions are[1]:

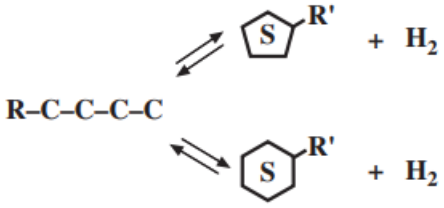
- **Dehydrogenation of naphthene**



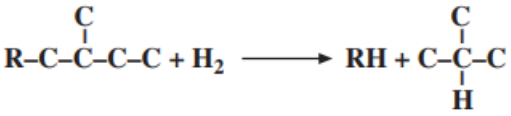
- **Isomerization of Paraffins and Naphthenes**



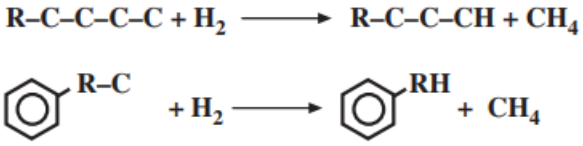
- **Dehydrocyclization of Paraffins**



- **Hydrocracking**

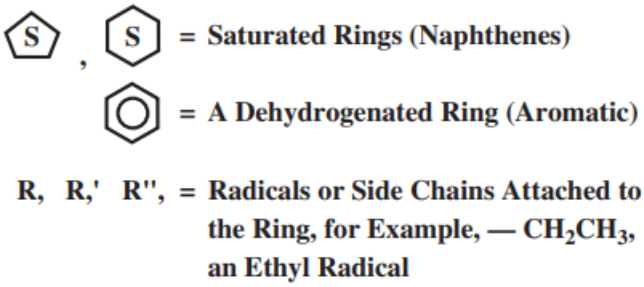


- **Demethylation**



- **Dealkylation of Aromatics**

- **Symbol key**



1.2.3 Fractionation Section

This section receives the feedstock from Reaction Section Product Separator (100-V-5). The purpose of the fractionation section is to split the (100-V-5) liquid product (Magnaformate) into LPG cut, C5 cut, C6 cut, C7 cut and C8+ cut, respectively. C6 cut will be routed to the Aromatics Recovery Unit (Unit 200) as feedstock to recover high purity benzene and toluene products. C8+ cut will be routed to Para-Xylene Recovery Unit (Unit 400) as feedstock to produce high-purity Para-Xylene product. LPG cut, C5 cut and C7 cut are routed to Gas plant, LNHT (Light Naphta Hydrocarbon treating unit, unit 700/702) and storage tank as final products respectively. 100-V-5 vapor product (magnaforming net gas) is also purified in the recontact section (Net gas absorbing and Rich Oil Stripping). The purified net gas is mainly sent to the HPU (Unit 900) and the balanced purified net gas is routed to Naphtha Hydrotreating Unit

(NHU) for hydrotreating the straight-run naphtha or used as fuel gas. The Platformate Splitter Section of 100 Unit is a fractionation section which receives major feedstock from existing Catalytic Reforming 2 Unit (Unit 103) and some of below C5 product from Isomerization Unit (Unit 500). The purpose of this section is to maximize the aromatics products within the Skikda Refinery complex. This section could be divided to seven systems:

- Magnaformate Stabilizer System (100-C-4 Column)
- Magnaformate Splitter System (100-C-5 Column)
- Magnaformate Toluene Splitter System (100-C-6 Column)
- Magnaformate C4/C5 Splitter System (100-C-7 Column)
- Magnaforming Net Gas Absorbing System (100-C-53 & 100-C-3 Columns)
- Platformate Splitter System (100-C-51 Column)
- Platformate Toluene Splitter System (100-C-52 Column)

1.3 Magnaformate Stabilizer System - 100-C-4 Column

The purpose of the magnaformate stabilizer (100-C-4) is to separate C5- cut from the Magnaformate. The objective is to minimize the C5- cut and maximize the benzene recovery in the bottom product. The benzene in net overhead product should be minimized. The magnaformate stabilizer (100-C-4) contains 39 valve type trays. There are three different feed locations available to adapt the different magnaformate compositions, at tray #16, tray #20 and tray #24, respectively. Normal feed tray is #20. The feed to column combines the magnaformate from 100-V-5, liquid from net gas separator(100-V-54), liquid from treated net gas separator (100-V-55) and overhead liquid product from 100-C-3 (rich oil stripper). After preheated in feed/bottom exchanger (100-E-70), the combined feed enters the column at tray #20 under normal operation. The heat input at the column bottom is from the magnaformate stabilizer reboiler (100-E-72). 100-E-72 is a horizontal thermosiphon type reboiler. MP steam is employed as heating medium to input the required duty. The flow of the MP steam to 100-E-72 is controlled by the temperature controller on the reboiler supply line. The overhead vapor of the column enters the air condenser (100-EA-54) followed by a trim cooler (100-E-59) using cooling water as cooling medium. The non-condensable is separated from the liquid in the receiver 100-V-6. The liquid from100-V-6 is pumped, through the reflux pump 100-MP-63A/B, back to 100-C-4 as reflux, and to magnaformate C4/C5 splitter as net overhead. The reflux flow is under local auto control, and the net overhead product withdraw is controlled by the 100-V-6 level control loop. The net bottom product leaves the column on flow control, which is reset by the bottom level control. The net bottoms is cooled in feed/bottoms exchanger (100-E-70) and sent to magnaformate splitter (100-C-5) for further processing. The pressure of the column is controlled by resetting the offgas flow from the receiver, 100-V-6. The high-high column overhead pressure will shut off the steam supply to 100-E-72. [9]

1.4 Octane Number

An octane number is a measure of the knocking tendency of gasoline fuels in spark ignition engines. The ability of a fuel to resist auto-ignition during compression and prior to the spark ignition gives it a high-octane number. The Octane Number of a fuel is determined by measuring its knocking value compared to the knocking of a mixture of n-heptane and isooctane (2,2,4-trimethyl pentane) [10].

There are two methods of measuring octane number of a fuel in the laboratory. The methods are known as Motor Octane Number (MON) and Research Octane Number (RON).

The motor octane number is indicative of high-speed performance (900 rpm) and is measured under the conditions of heavy road use. The research octane number is indicative of normal road performance under low engine speed (600 rpm) city driving conditions. The third type of octane number is defined as posted octane number (PON), which is the arithmetic average of the MON and RON. Thus:

$$\mathrm{PON} = [(\mathrm{MON} + \mathrm{RON})/2]$$

Generally, iso-paraffin derivatives have higher octane number than do normal paraffin derivatives. Naphthene derivatives have relatively high-octane number than the corresponding paraffin derivatives e aromatic derivatives also have very high-octane numbers, so that one of the major operations of a petroleum refinery is to convert straight-chain hydrocarbons to branched-chain alternatives. Arbitrarily, pure iso-octane (2,2,4-trimethylpentane) is accorded a research octane number of 100, while the straight-chain paraffin *n*-heptane is given an octane number of zero. Petrol is made up of a mixture of mostly branched-chain paraffins, with suitable additives, to give a RON in the range 90–100. Typically, 'regular' grade petrol in the UK will have an octane number of up to about 95, whereas 'premium' grade will lie in the range 95–100. The choice of which fuel to use depends on the engine. Originally, lead tetraethyl was added to delay the onset of self-ignition. When the extreme toxicity of organic lead became clearly established, it was replaced by less harmful additives such as methyl tertiary-butyl ether (typically known as MTBE) [11].

The octane number of a fuel can be predicted by using principal component regression of chromatographic data but the test methods based on spectroscopic techniques such as near-infrared (NIR), infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) are applied for the measurement and/or prediction of octane numbers and other parameters of gasoline and are preferred.

Application of any such test methods to gas condensate or natural gasoline may have a limited value if the gas condensate or natural gasoline is a very minor constituent of the gasoline blend. In such a case, the gas condensate or natural gasoline may only be a complementary constituent to make up the final blend for sales gasoline and the octane number would have little, if any, effect, on the octane number of the final blend [10].

1.5 Reid vapor pressure

The Reid vapor pressure (RVP) of a product is the vapor pressure determined in a volume of air four times the liquid volume at 37.8 °C (100 °F). This property measures the vapor-lock tendency of a motor gasoline in which excessive vapors are produced in the fuel line causing interruption of the supply of liquid fuel to the engine. It also indicates the explosion and evaporation hazards of the fuel. One of the standard tests is ASTM D323 [12].

The Reid vapor pressure differs from the true vapor pressure of the sample due to some small sample vaporization and the presence of water vapor and air in the confined space. However, this

test method (ASTM D323) is not applicable to liquefied crude oil gases or fuels containing oxygenated compounds other than methyl *t*-butyl ether (MTBE) and other test methods are recommended.
The latter test method (ASTM D5191) describes the use of automated vapor pressure instruments to determine the total vapor pressure exerted in vacuum by air-containing, volatile, liquid crude oil products, including automotive spark-ignition fuels with or without oxygenates. This test method is suitable for testing samples with boiling points above 0 °C (32 °F) that exert a vapor pressure between 7 kPa and 130 kPa (1.0 psi and 18.6 psi) at 37.8 °C (100 °F) at a vapor-to-liquid ratio of 4:1 – these parameters are typically applicable to gas condensate and natural gasoline[10] .

RVP is not an additive property. Therefore, RVP blending indices are used. A commonly used RVP index is based on an empirical method developed by Chevron Oil Trading Company (1971) [10].

$$BI_{RVPi} = RVP_i^{1.25}$$

where BI_{RVPi} is the RVP blending index for component i and RVPi is the RVP of component i in psi. Using the index, the RVP of a blend is estimated as:

$$BI_{RVP,Blend} = \sum_{i=1}^{n} x_{vi} BI_{RVPi}$$

where x_{vi} is the volume fraction of component i.[1]

2.1 Characterization of 100-C-4 feed composition using ASTM Distillation D86

ASTM Distillation D86 is a basic test method used for the determination of boiling range of a petroleum product by performing a simple batch distillation. This technique, is one of the longest-standing test methods overseen by ASTM Committee D02[13].

2.1.1 Description of the ASTM D86 test method

100 ml of the product is heated in a standard flask and the different evaporated fractions are collected after passing through a condenser. The operating procedure specifies a limit for the distillation rate of 4 to 5 ml per minute to ensure that the results are reproducible with the precision defined by the standard. The initial boiling point (IBP) is the temperature at which the first drop falls into the test tube. The temperatures are then recorded for the percentages of distillate collected (5%-95%). At the end of the distillation, only the temperature variation is monitored. It passes through a maximum and then decreases due to cracking of the residual fraction in the flask. This maximum is called the final boiling point (FBP) of distillation. The total fraction collected in the test tube is then measured; also the residue in the flask should be measured after cooling. The volumetric balance by difference with the initial volume of the sample gives a certain percentage of losses attributable to the light constituents (C3, C4 and C5) which are distilled at the beginning of the operation and pass through the condenser without condensing[10].

The total volume collected in the test tube constitutes the distillate, which must be cooled before taking a reading. After cooling, the volume of liquid residue in the flask is measured in a graduated test tube in tenths of a ml. 100ml - (distillate + residue) = losses [10].

2.1.2 Importance of the test

In the case of gasoline, the presence of light fractions favors cold starts by ensuring sufficient vaporization. Too high a final boiling point would lead to incomplete combustion, forming deposits and causing auto-ignition. The distillation test therefore enables the performance of distillation units to be monitored by comparing actual results with desired results, helping refiners to identify and correct problems. In addition, it ensures that products comply with specifications by checking that products meet the desired boiling range and other criteria. [13]

2.2 Characterization of 100-C-4 feed composition using gas chromatography

To determine the composition of the reformate recovered from the different streams, we began by identifying the components contained in the hydrocarbon mixture. To do this, a sample of this

mixture was analyzed by the ASTM D6729-01 which is standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Meter Capillary High Resolution Gas Chromatography.

This method is used for the determination of individual hydrocarbon components of gasoline and light liquid hydrocarbon mixtures encountered in petroleum refining operations.

This procedure is applicable to samples containing less than 25 mass % of olefins. Based on study results, individual component concentrations and precision are determined in the range of 0.01 to approximately 30 mass %. The procedure may be applicable to higher and lower concentrations for the individual components. [14]

2.3 Presentation of Aspen Hysys

Aspen HYSYS (from Hygrotech & Systems) is a comprehensive process modeling software developed by AspenTech, it is widely used in the oil and gas, refining, and chemical industries. It provides robust simulation capabilities for designing, optimizing, and analyzing various processes, enabling engineers to improve efficiency, safety, and profitability.

Aspen HYSYS allows for the detailed simulation of complex processes and equipment such as distillation, heat exchange, absorption and chemical reactions. Hysys includes a vast library of thermodynamic models and property packages that ensure accurate predictions of physical and chemical properties. In our study, the software was used to conduct a full analysis in order to understand the impact of variable changes on process performance to finally make an optimization.

2.4 Oil characterization by Aspen Hysys

The Oil Manager tool in Aspen Hysys has the ability to transform complex petroleum mixtures into a series of discrete hypothetical components. These petroleum hypo components provide the basis for the property package to predict the remaining thermodynamic and transport properties necessary for fluid modeling.

HYSYS produces a complete set of physical and critical properties for the petroleum hypocomponents with a minimal amount of information. However, the more information we supply about the fluid, the more accurate these properties will be, and the better HYSYS will predict the fluid's actual behavior[15].

2.5 Simulation steps for the design case

2.5.1 Step 1: Introducing the feed compositions and characteristics

❑ List of components

For the initial development phase of our process simulation via Aspen HYSYS, it was imperative to translate the constituents of the material balance, which were presented in generic terms such as n-Naphthenes or n-paraffins, into their specific chemical components. Each component was represented by one or more molecules belonging to the same family. This process of converting general classifications into specific chemical entities was fundamental to establishing a realistic and reliable simulation framework. The list of components is shown in the table below.

Table 2.1. List of components

	Components as described in the material balance	Component list introduced in Aspen HYSYS simulation
Hydrogen	Hydrogen	H_2
C4- HC Lights	C4- HC Lights	Methane
		Ethane
		Propane
		i-butane
		n-butane
C5+ HC	Paraffins C5	i-pentane
		n-pentane
	Naphthenes C5	Cyclopentane
	Paraffins C6	n-Hexane
	Naphthenes C6	Cyclohexane
	Paraffins C7	n-heptane
	Naphthenes C7	Cycloheptane
	Paraffins C8	n-octane
	Naphthenes C8	Cyclooctane
	Paraffins C9	n-Nonane
	Naphthenes C9	Cyclononane
	Paraffins C10	n-Decane
	Total olefins	i-Butene
		Cis2-Pentene
	Benzene	Benzene
	Toluene	Toluene

	M-Xylene	M-Xylene
	O-Xylene	O-Xylene
	P-Xylene	P-Xylene
	Ethylbenzene	E-Benzene
	Aromatics C9	n-Pbenzene
		135-Mbenzene
	Aromatics C10	i-Bbenzene
		n-Bbenzene
	Indane	Indane

2.5.2 Step 2: The thermodynamical model

The Peng-Robinson model excels in liquid density prediction, especially for non-polar compounds. We chose it for two main reasons: its high accuracy over a wide range of temperatures and pressures, and its special treatment of key components.[16]

2.5.3 Step 3: Entering the simulation environment:

This step consists of entering the simulation environment in which we define the feeds composition and conditions and all the equipment as specified by the manufacturer in the material balances, the stream summary, the process flow diagram and the process datasheets of the equipment. All the data needed for this step is available at the appendix of the documents and this include:

- Feed compositions
- Feed conditions
- Datasheet of the 100-C-4 column
- Datasheet of 100-E-70 heat exchanger

2.5.4 Step 4: Simulation of 100-E-70 heat exchanger

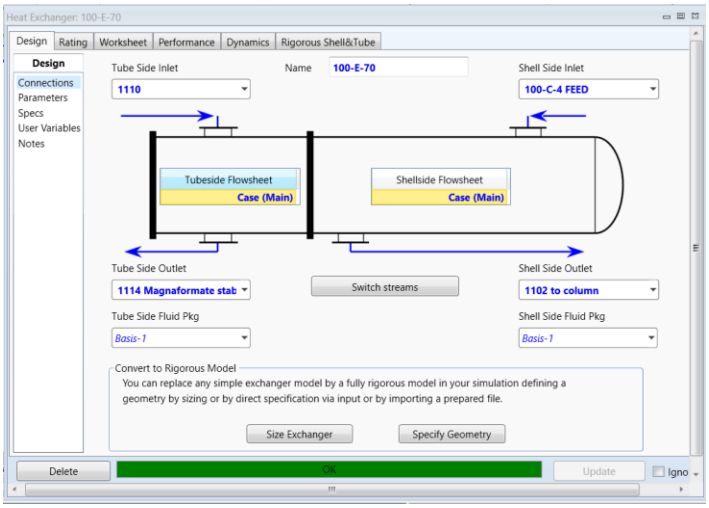


Figure 2.1. Heat exchanger configuration

2.5.5 Step 5: Simulation of 100-C-4 distillation column

In our case, Aspen HYSYS will be associated with a simplified model, which will facilitate calculations and avoid convergence problems. The system, comprising a distillation column and an overhead product condensation system with an air cooler followed by a heat exchanger and reflux drum, will be simplified to a system with a condenser only. To ensure the reliability of the model, the design results must be consistent with those obtained by simulation. The model used is a simple distillation column with a usual Hysys reboiler and the column was customized as follow:

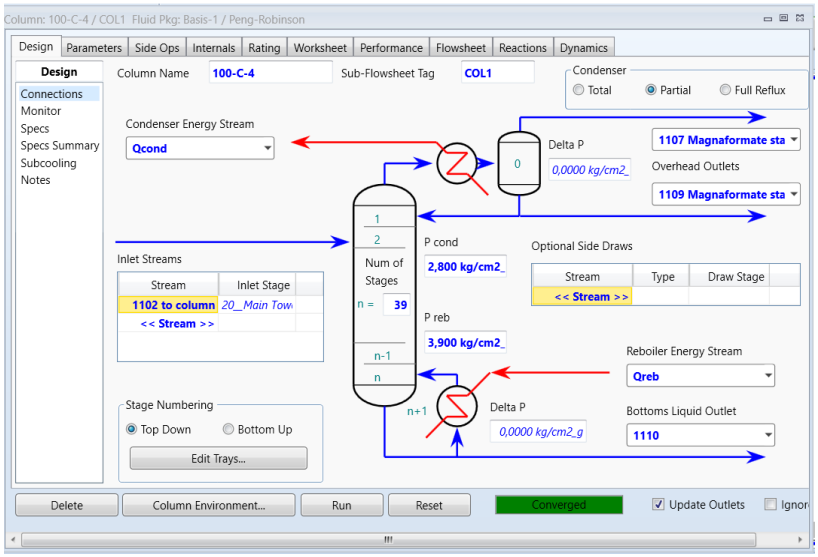


Figure 2.2. 100-C-4 column design (Design case)

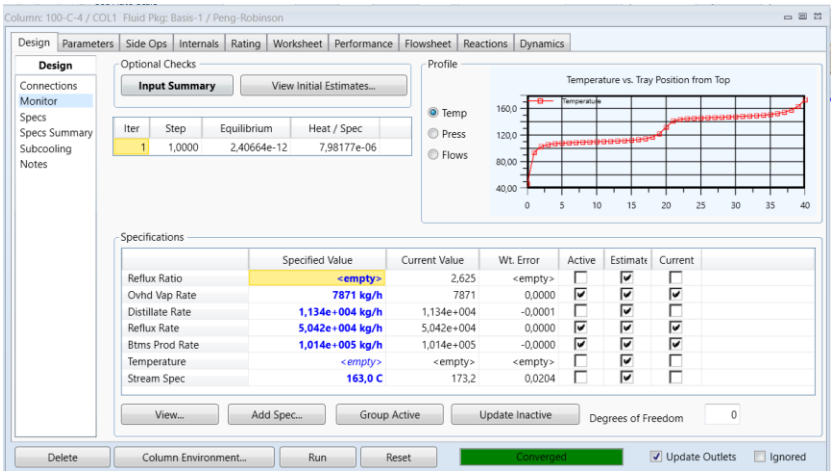


Figure 2.3. 100-C-4 Monitor (Design case)

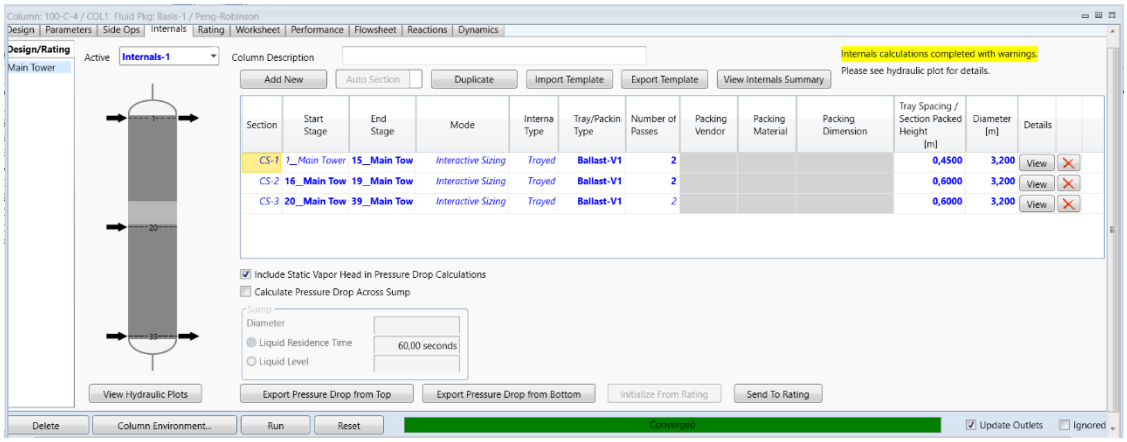


Figure 2.4. 100-C-4 Column internals

2.5.6 The resulting flowsheet of the design case

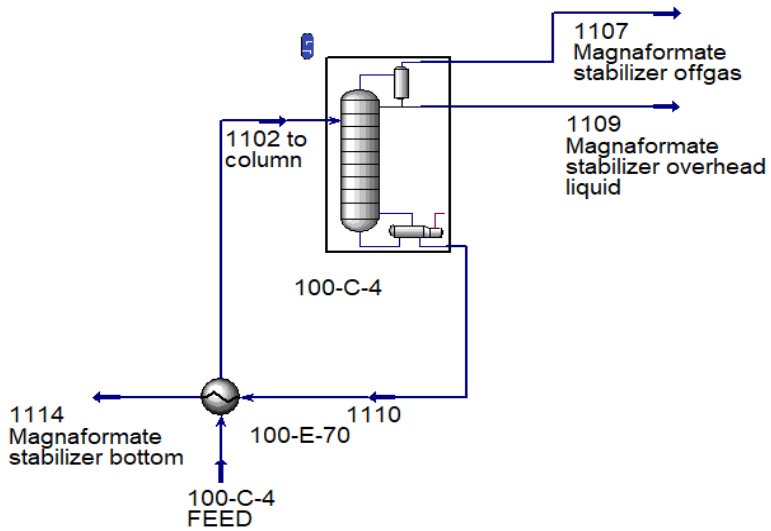


Figure 2.5. Simulation of Magnaformate Stabilizer System (100-C-4 Column)

2.5.7 Review and validation of the simulation model

In order to validate our simulation, we have carried out comparisons between the design values and the simulation values, for a user defined stream (stream 1102) and a stream calculated by Hysys (stream 1114). The results are presented in the following two tables.

Table 2.2. Stream 1102 Specifications

	Design	Simulation
Molecular weight	87,81	87,4
Molar flow [Kgmole/h]	1373,2	1380
Std Ideal Liq Vol Flow [m3/h]	156,02	156
Liq density (std) [Kg/m3]	769	773

Table 2.3. Stream 1114 specifications

		Design	Simulation
Properties	Molecular weight	96,44	98
	Std Ideal Liq Vol Flow [m3/h]	123,97	122,44
Composition (mass fractions)	Benzene	0,116	0,106
	Toluene	0,2349	0,258
	Xylenes	0,2303	0,252
	Aromatics C10	0,0076	0,008

From the results grouped in Table 2.2, it was found that the calculated results are almost identical to those obtained by the designer. This means that the list of selected components and the thermodynamic model are consistent with those chosen by the designer. Also, the results presented in Table 2.3 show that the column properties and product composition are closely aligned, indicating that the simplified distillation column model is reliable and accurately reflects the design case. Consequently, this model can be used for further calculations.

2.6 Simulation of the real case

2.6.1 Step 1: Selection of components and thermodynamical model

The components were selected based on the gas chromatography analysis of the sample. The selected list is shown in table 2.4. The chosen thermodynamical model is Peng Robinson.

Table 2.4. Component list of the real case product

Pure components		
Propane	n-Nonane	n-Hexane
Benzene	4-Moctane	3-Mpentane
Toluene	n-Octane	n-Pentane
Cis2-Pentane	3-Mheptane	i-Pentane
Cyclopentane	n-Heptane	n-Butane
n-Decane	3-Epentane	i-Butane

2.6.2 Step 2: Characterization of the U100 reformate oil

This step includes three different stages:

(A) Characterization of the assay: essay characteristics are shown in figures 2.2, 2.3, and 2.4.

(B) Generation of hypotheticals: This step came after the configuration of the essay, we click on "output blend" and then Hysys will perform the calculation and generates hypotheticals and its properties such as: Normal boiling point, the molecular weight and the density. The generated hypotheticals are shown in figure 2.5.

(C) Installation of the oil in the flowsheet: Once we generate the hypotheticals or the oil blending, we press on "Install Oil". this step will allow us to transfer the hypocomponent information into the flowsheet.

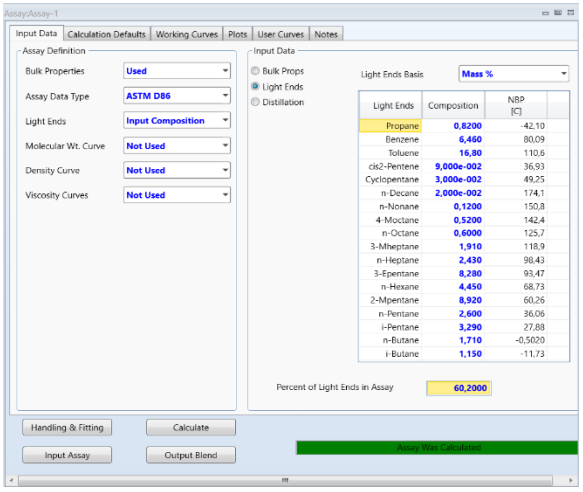


Figure 2.6. Light ends composition

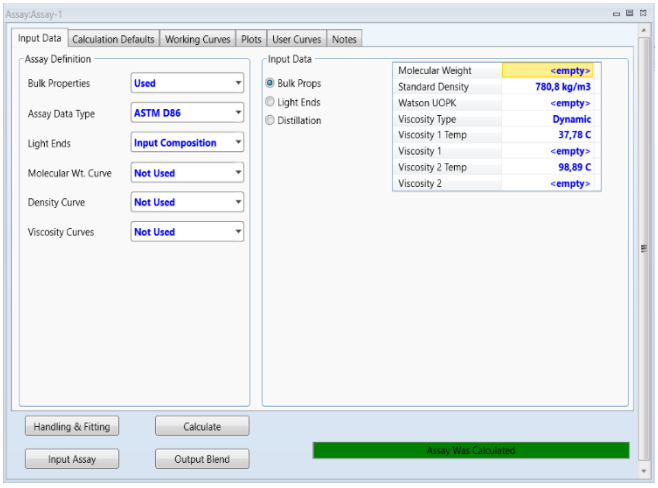


Figure 2.7. Bulk properties

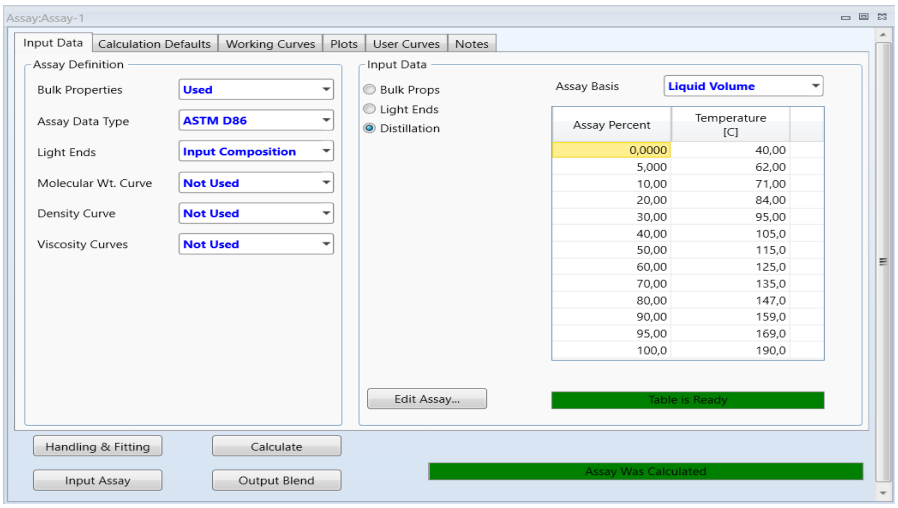


Figure 2.8. Distillation curve

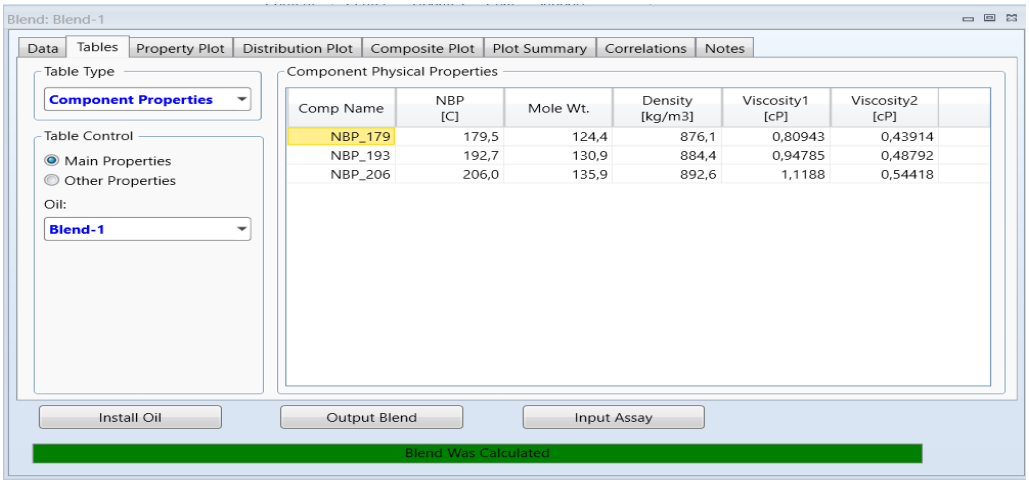


Figure 2.9. Generated hypothetical/ Blending oil

2.6.3 Step 3: Entering the simulation environment

In this stage, we will introduce the necessary equipment. In our case, we have only introduced an exchanger and a distillation column. The heat exchanger was introduced exactly like the previous part, but the distillation column was configurated in a different way. According to the real case specifications, except the column internals.

2.6.4 Step 4: Personalization of the distillation column specifications

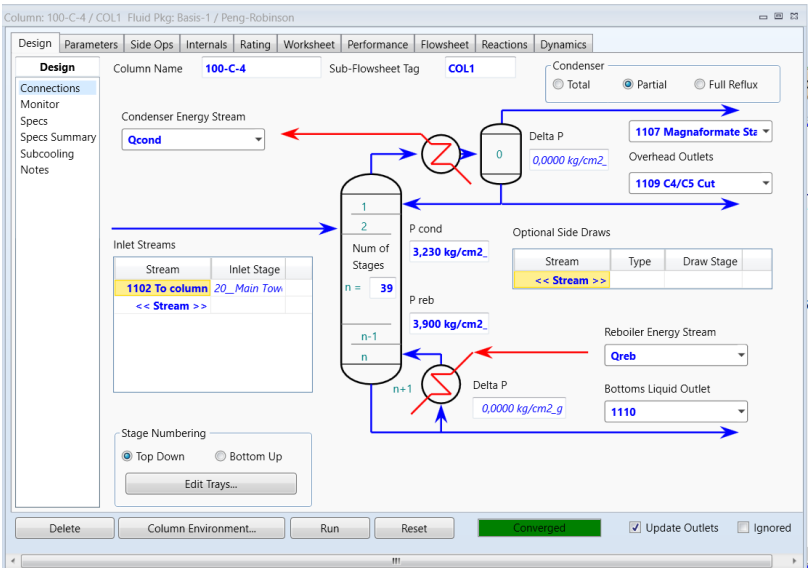


Figure 2.10. Design of the distillation column

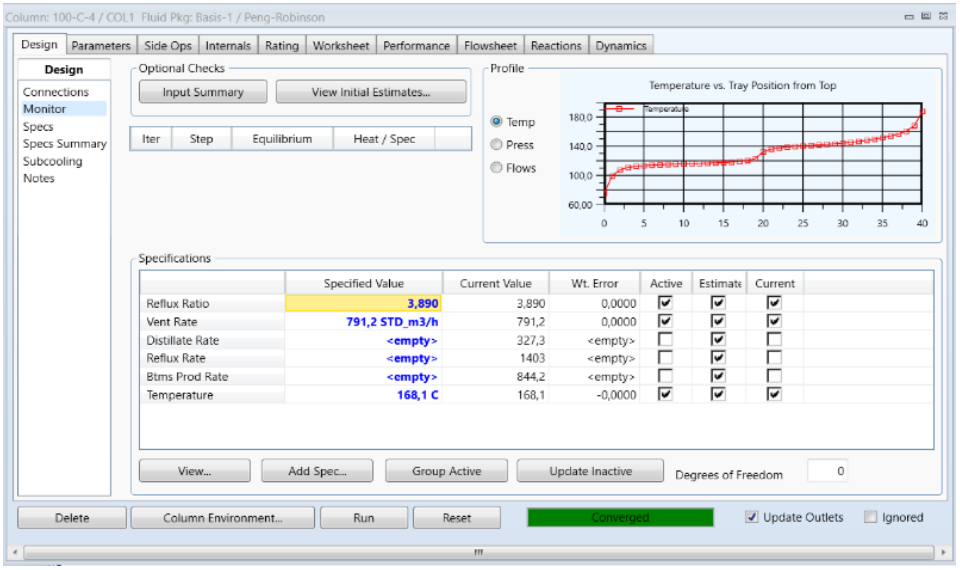


Figure 2.11. The distillation column monitor

2.6.5 Step 5: Adding the adjuster

The ADJUST function in Aspen HYSYS acts as a control mechanism to achieve the desired result in the process model. It allows you to specify a target variable in the process flow or business unit you wish to control, and then define the desired value for this variable. This value can be numerical or a reference to another variable in the model.

The ADJUST function ensures that the simulation converges towards a stable solution by forcing a specific variable to fulfill a defined condition.

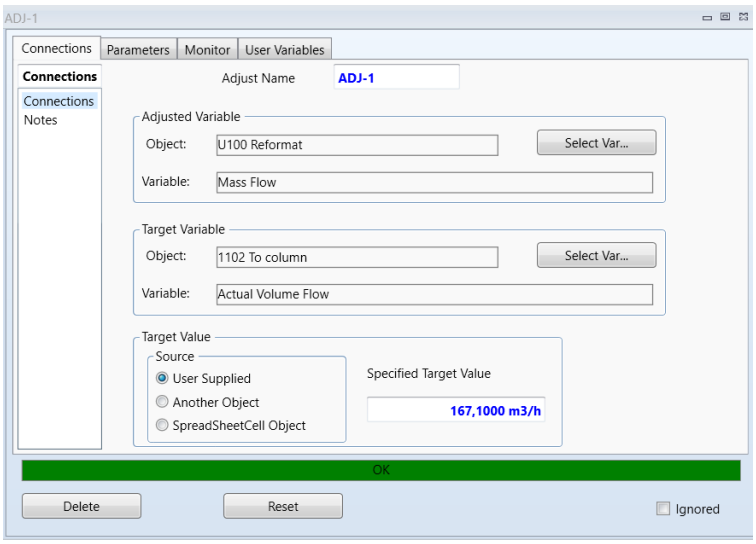


Figure 2.12. The adjuster

2.6.6 The resulting flowsheet of the real case

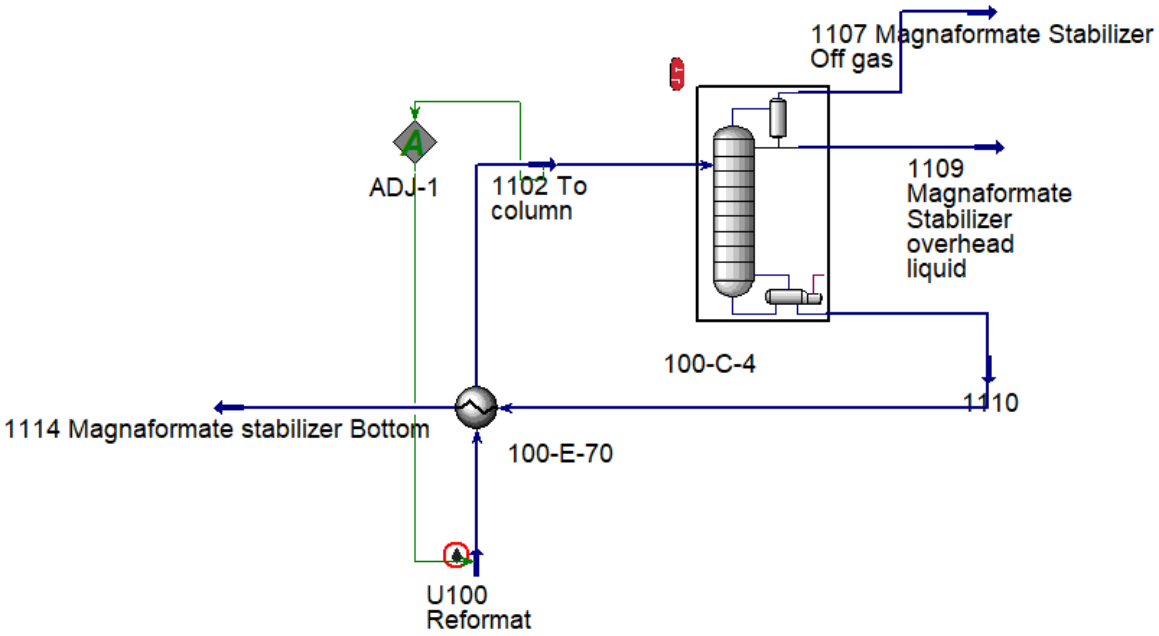


Figure 2.13. Simulation of Magnaformate Stabilizer System (100-C-4 Column) in the real case

Chapter 3: Results and discussion

3.1 Introduction

This section presents the findings and interpretations of the characterization analyses conducted on the fluid and the case studies performed using Aspen HYSYS. The characterization analyses provided insights into the physical and chemical properties of the fluid, while the Aspen HYSYS simulations enabled the evaluation of the fluid's behavior and composition under various process conditions.

3.2 Results of the ASTM D86 Distillation

The results obtained are shown in the figure below:

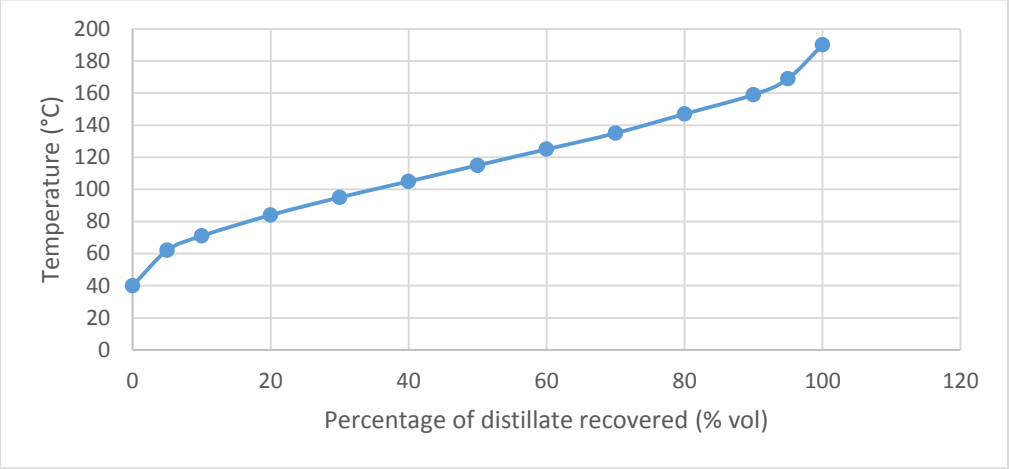


Figure 3.1. ASTM D86 Distillation curve of gasoline

The test results revealed that the initial vaporization point, occurring at 0% volume, was 40°C. The distillation process reached its final boiling point (FBP) at 190°C.

3.3 Results of the ASTM D6729 Gas chromatography

The results obtained from the ASTM D6729 gas chromatography test are presented in the table 3.1.

Table 3.1. Results of the ASTM D6729 Gas chromatography

Component	composition
Propane	0.82
Benzene	6.46
Toluene	16.8
cis2-Pentene	9.00E-02
Cyclopentane	3.00E-02
n-Decane	2.00E-02
n-Nonane	0.12

4-Moctane	0.52
n-Octane	0.6
3-Mheptane	1.91
n-Heptane	2.43
3-Epentane	8.28
n-Hexane	4.45
2-Mpentane	8.92
n-Pentane	2.6
i-Pentane	3.29
n-Butane	1.71
i-Butane	1.15
Total light ends (%)	60.2

3.4 Oil characterization

Based on the information provided to the Hysys Oil Manager, including the results of distillation (D86) and chromatography (ASTM D6729), the following data was obtained for the feed stream of column 100-C-4, as shown in the table below.

Table 3.2. 100-C-4 Feed Composition and Boiling temperatures

Components	Mass fraction (%)	Boiling Temperature (°C)
Propane	0.82	-42
Benzene	6.46	80
Toluene	16.80	111
cis2-Pentene	0.09	37
Cyclopentane	0.03	49
n-Decane	0.02	174
n-Nonane	0.12	151
4-Moctane	0.52	142
n-Octane	0.60	126
3-Mheptane	1.91	119
n-Heptane	2.43	98
3-Epentane	8.28	93
n-Hexane	4.45	69
2-Mpentane	8.92	60
n-Pentane	2.60	36
i-Pentane	3.29	28
n-Butane	1.71	-1

i-Butane	1.15	-12
NBP[0]179*	21.64	179
NBP[0]193*	10.60	193
NBP[0]206*	7.56	206

It has been observed that HYSYS introduced three hypothetical components with normal boiling points of 179°C, 193°C, and 206°C respectively, and estimated their concentrations within the mixture.

By observing the composition of the feed, we notice that the feed contains a mass fraction of light components (having a boiling temperature of less than 69°C) equal to 23,06%. This fraction should be set to the lowest possible value in the Magnaformate Stabilizer (100-C-4).

3.5 Influence of variation of feed position on the bottom product composition

The designer mentions the possibility of changing the feed stage without indicating the effect on the product composition. Our objective was to determine the effect of varying the feed stage on the product composition. To this end, 3 simulations were carried out based on the design case simulation using Aspen Hysys software by varying the feed stage between tray 16, tray 20 and tray 24. The results show that the mass fractions of all components except benzene and n-hexane are identical.

Table 3.3 shows the improvement in the benzene mass fraction and the elimination of the n-hexane mass fraction (%) when the feed position was changed (from tray 16 to tray 20 and tray 24 respectively). There was an increase in the benzene mass fraction measured when the feed position was changed from 16 to 20 and 24, while the n-hexane mass fraction decreased.

Table 3.3. Influence of variation of feed position on the recoveries of n-Hexane and benzene.

	Tray 16	Tray 20	Tray 24
Benzene mass fraction improvement (%)	+5.31	+6.11	+6.70
n-Hexane mass fraction removal (%)	-44.46	-45.36	-45.95

3.6 Effect of stage 39 temperature

To explore how varying the 39th stage temperature affects on benzene recovery and the removal of light components, we focused on benzene, 2-Mpentane, n-Hexane, and the mass fraction of heavier hydrocarbons (the generated hypotheticals) as key parameters. We analyzed their changes across a temperature range from 167°C to 171°C (Figure 3.3) and compared these findings with those from the column operating at a 169°C on stage 39.

Upon comparing the data in Table 3.4 and the trends shown in Figure 3.1, it is evident that raising the temperature of the 39th stage from 167°C to 171°C yields positive outcomes for

benzene recovery and the elimination of light components such as 2-methylpentane and n-hexane.
Increasing the temperature to 170,5°C allow a complete elimination of 2-methylpentane and a significant reduction in the n-hexane fraction; however, when the temperature exceeds 170.5°C, significant benzene losses start to occur. Therefore, it is not recommended to heat beyond this temperature.

Table 3.4. Influence of reboiler temperature.

		Actual case	Design temperature			
Stage 39 Temperature (°C)	167	168	169	170	170,5	171
Reboiler temperature (°C)	186	187.9	188	189.6	189,9	190
2-Mpentane	0,0008	0.0005	0.0003	0.0001	0	0
n-Hexane	0,018	0.0121	0.0077	0.0034	0,0014	0.0005
Benzene	0,0751	0.0744	0.0736	0.0722	0,0706	0.0672
Heavy HC	0,5117	0.5156	0.5187	0.5220	0,524	0.5265

3.7 Effect of reflux ratio

In this part, the effect of reflux ratio was studied by varying it from 1.89 to 7.89. The results of the mass fraction of benzene, 2-Mpentane, n-Hexane, and the heavy HC for each ratio are represented in Table 3.5.
Upon analyzing the results presented above, it was observed that as the reflux ratio increases, there is a decrease in the concentration of 2-Mpentane and n-Hexane in the final product. At higher reflux ratios, these components are more likely to evaporate and be collected in the distillate. Conversely, the concentrations of Benzene and Heavy HC slightly increase with an increase in reflux ratio.
Therefore, increasing the reflux ratio leads to better removal of light components (2-methylpentane and n-hexane). Overall, a higher reflux ratio facilitates improved separation of components. It's important to note that higher reflux ratios can reduce the yield of distillate because more volatile components are recycled within the column rather than being collected as product.

Table 3.5. Effect of reflux ratio

Reflux ratio	1,89	2,89	3,89	4,89	5,89	6,89	7,89
2-Mpentane	0,0053	0,0019	0,0008	0,0004	0,0003	0,0002	0,0001
n-hexane	0,0270	0,0229	0,0182	0,0142	0,0108	0,0083	0,0063
Benzene	0,0698	0,0736	0,0751	0,0759	0,0764	0,0766	0,0768
HC	0,5070	0,5092	0,5116	0,5136	0,5153	0,5166	0,5177

3.8 Optimization of the 100-C-4 stripping system

Aspen Hysys was used to optimize the 100-C-4 stripping system, which is our main objective. To this end, the effects of feed stage position, reboiler temperature and reflux ratio were investigated in the previous sections. From the results presented in the previous sections, it is clear that modifying the feed stage position doesn't have an important effect on the desired product (3.1. The influence of feed stage position), and since our main objective is to separate the C5- cut and 2-Mpentane from the magnaformate and to maximize the benzene recovery in the bottom product. In the actual case, we only take into account the temperature and reflux ratio as key parameters.

Then, we carried out two simulations of the magnaformate stabilizer column. In the first one, by changing the temperature to 170°C, we have reached an elimination of light hydrocarbons equal to 99.95%. In addition to that, the modification will allow us to reach 52.2% of heavy hydrocarbons mass fraction while the benzene mass fraction decreases by a slight percentage to 7.22% of benzene. The results presented in Table 3.5 demonstrate the effectiveness of the conducted analysis.

In the second simulation, by changing the reflux ratio to 7.89, we have reached a mass fraction of 2-Mpentane equal to 0.0001 which is the same found by setting the temperature at 170°C. To conduct a process optimization, we must employ economic reasoning to identify the most suitable parameter for optimization.

3.8.1 Economic evaluation of the optimization process

In order to study the economic impact of temperature and reflux ratio variation in our process. We calculate the power required at each level of temperature and reflux ratio (Qrequired). This allows us to estimate the costs associated with the process. Tables 3.6 and 3.7 show the results obtained.

By comparing the results obtained in Table 3.6 and Table 3.9, it is clearly seen that the energy required to increase the reflux ratio is much higher than the energy required to increase the temperature. Therefore, we choose to optimize our column by modifying the temperature instead of the reflux ratio, as our economic evaluation should focus on identifying the parameter that

minimizes the total cost and provides the desired composition of our product. It was concluded that temperature variation was the most economical modification as it balanced process efficiency with energy consumption costs.

Table 3.6. The power required for each temperature

Temperature (°C)	**167**	**170**
Qcond (kW)	12800.13	13748.93
Qreb (kW)	17080.01	19287.18
Qrequired (kW)	29880.14	33036.11

Table 3.7. The power required each reflux ratio

Reflux ratio	**3,89**	**7,89**
Qcond (kW)	13153.9	24509.2
Qreb (kW)	18651.2	30013.59
Qrequired (kW)	31805.1	54822.79

3.8.2 Limitations of the simulated optimization and considerations for the real case

The results obtained in the previous section only remain in the simulation of the design case and don't correspond to the real case. So, it's important to acknowledge limitations before real-world implementation.

The energy requirements of the cooling system, such as the electric power used for the aero-refrigerant and the high-water flow rates needed in the heat exchanger should be taken into consideration in the analysis. In addition, the energy consumption of the pumping system in the heat exchanger and for heating in the reboiler must also be included in the cost calculation.

The effect on product properties such as the octane number should also be taken into account during the separation process. Eliminating the 2-Mpentane and n-hexane will improve the octane number of the final product, also, these components will be sent to the isomerization unit (U700) and will be turned to a more valuable products such as benzene by the isomerization process.

General Conclusion

The aim of this project was to simulate and optimize the stripping system of Magnaforming unit (U100) at Skikda's refinery 1 by using analysis methods for characterizing petroleum products, including ASTM D86 distillation and ASTM D6729 gas chromatography, coupled to numerical methods for characterizing petroleum mixtures and modeling the unit operation used (distillation) through simulation using Aspen HYSYS software. The ultimate goal of the study is to find the optimal solution to improve the gasoline quality by improving its RON.

Indeed, the effects of feed stage position, reboiler temperature and reflux ratio have been studied. It is acknowledged that the (100-C-4) stripping system is designed to totally eliminate light hydrocarbon fraction which is characterized by its components low boiling points, the function of the system is to maximize the recovery of the benzene in the bottom product.

The analysis of (100-C-4) feed by the ASTM D86 Distillation method shown that the reformate before stripping, distills between 40°C and 190°C. The results of gas chromatography using the ASTM D6729 revealed that the reformate is composed of 23.06% of light hydrocarbons including n-hexane and 2-Mpentane. The real case conditions have shown that the column is operating at a reflux ratio equal to 3.89 and temperature equal to 167°C at the 39^{th} stage. The results of the simulation based on these real conditions have shown that the composition of the bottom product contains a mass faction of 2-Mpentane equal to 0.08% and a n-hexane fraction equal to 1.8% thus confirming that the reduction marked in the researched octane number is due to the presence of the 2-Mpentane in the bottom product. This unsatisfactory result led us to look for the optimal conditions to totally eliminate this molecule.

After experimenting with different feed positions in the distillation column, according to the designed case data, it was found that varying the feed location primarily impacts the concentrations of benzene and n-hexane. Optimal concentrations were achieved with benzene highest and n-hexane lowest when the feed was introduced at stage 24. Currently, in the actual scenario, the feed is situated at stage 20, and based on these results, there is no necessity to relocate it.

In the second phase of our study, we investigated the effect of temperature on the bottom product by varying the temperature at stage 39 from 167°C to 171°C. Our findings indicate that the optimal temperature is 170.5°C. At this temperature, we were able to completely eliminate 2-Mpentane and significantly reduce the concentration of n-hexane in the bottom product. Furthermore, this temperature allowed us to achieve a satisfactory Benzene concentration of 7.06% and a heavy hydrocarbons mass fraction of 52.4%.

The results from our temperature variation study underscore the critical importance of this parameter in distillation processes. Even slight fluctuations in temperature can significantly

impact product quality and lead to losses of valuable components like Benzene. Therefore, maintaining precise and stable temperature control within distillation columns is crucial, necessitating the use of advanced control systems to optimize performance and maximize product yield.

In the third part of our study, we explored the impact of varying the reflux ratio. Our findings indicate that increasing the reflux ratio improves the overall product quality; however, it does not achieve complete elimination of 2-Mpentane. Additionally, we analyzed the energy consumption aspects by calculating the duties in the condenser (Q_{cond}) and the reboiler (Q_{reb}). It became evident that increasing the reflux ratio does not present an economically favorable solution.

Considering both the product quality and energy consumption factors, we decided to maintain the reflux ratio at its initial value. This decision ensures a balanced approach where product quality is optimized without incurring excessive energy costs, thereby supporting a more sustainable and economically feasible operation.

The choice to optimize our column by modifying the temperature rather than the reflux ratio is due to our economic evaluation which indicated that we should focus on identifying the parameter that minimizes the total cost and provides the desired composition of our product. It was concluded that temperature variation was the most economical modification as it balanced process efficiency with energy consumption costs.

This simulation and optimization process proved to be invaluable in enhancing the composition of the final product from the distillation tower. It effectively optimized the concentrations of both light and heavy components based on their respective boiling points, leading to significant improvements in product quality and operational efficiency.

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