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Theoretical study on the hydrocracking of heavy distillates and simulation using HYSYS software

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DEDICATIONS

- FIRST OF ALL, I DEDICATE THIS MODEST WORK TO MY VERY DEAR PARENTS,

- MY DEAR SIBLINGS, FOR THEIR SUPPORT AND ENCOURAGEMENT.

- TO ALL MY FAMILY, MY LOVED ONES AND TO THOSE WHO GIVE ME LOVE AND VIVACITY, AS WELL

- TO MY COLLEAGUE FOR HIS MORAL SUPPORT, HIS PATIENCE AND HIS UNDERSTANDING THROUGHOUT THIS PROJECT.

- TO ALL MY FRIENDS WHO HAVE ALWAYS ENCOURAGED ME, AND TO WHOM I WISH MORE SUCCESS. AND TO ALL THE PEOPLE WHO SUPPORT ME AND FOR THE ADVICE THEY GIVEN ME

BENISSAD MOHAMMED HAYTHEM

DEDICATION

IN MY CAPACITY AS A ONE OF THE WRITERS OF THIS THESIS, I DEDICATE

IT TO:

MY **PARENTS** FOR EVERYTHING THEY HAVE DONE FOR ME, AND MY

FAMILY MEMBERS FOR SUPPORTING ME.

EVERYONE WHO HELPED US FINISH THIS PROJECT, ESPECIALLY MY

FRIENDS.

FINALLY, WE CONGRATULATE **MY COLLEAGUE** ON COMPLETING THIS

WORK IN A FAVOURABLE.

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succeed this work.

Abstract

In the petroleum industry, key processes include separation, conversion, upgrading, and purification. These processes are crucial for obtaining high-quality products that meet human, transportation, and environmental requirements. Among the separation processes, catalytic cracking is used to convert hydrocarbons into lower molecular weight compounds.

When hydrogen gas is injected during catalytic cracking, the process becomes hydrocracking, which offers several advantages over traditional catalytic cracking. Hydrogen ensures rapid expansion, increases catalytic activity, and allows for operation at lower temperatures and with greater selectivity. Furthermore, with the presence of hydrogen, coke deposition and catalyst deactivation are negligible.

The objective of our work is to conduct a comprehensive theoretical study on hydrocracking, using atmospheric residue from the distillation column as the feedstock. We aim to validate our findings by performing a simulation using HYSYS software.

The specific goals of our work are as follows:

- Propose the implementation of a hydrocracking unit in the HASSI MESSAOUD refinery.

- Utilize atmospheric residue from the distillation column to obtain lighter products.

- Increase the quantity of lighter products obtained.

- Achieve high-quality products selectively while reducing costs.

- Establish a cost-effective hydrocracking unit that produces desirable products.

Key Words :

atmospheric distillation , hydrocracking , cracking catalytic , petroleum products , HYSYS program .

الملخص

في صناعة البترول ، تشمل العمليات الرئيسية الفصل والتحويل والترقية والتنقية. هذه العمليات ضرورية للحصول على منتجات عالية الجودة تلبي متطلبات الإنسان والنقل والبيئة. من بين عمليات الفصل ، يتم استخدام التكسير التحفيزي لتحويل الهيدروكربونات إلى مركبات ذات وزن جزيئي أقل.

عندما يتم حقن غاز الهيدروجين أثناء التكسير التحفيزي ، تصبح العملية تكسرا بالهيدروجين ، مما يوفر العديد من المزايا مقارنة بالتكسير التحفيزي التقليدي. يضمن الهيدروجين تمددا سريعا ، ويزيد من النشاط التحفيزي ، ويسمح بالتشغيل في درجات حرارة منخفضة وانتقائية أكبر. علاوة على ذلك ، مع وجود الهيدروجين ، فإن ترسب فحم الكوك وتعطيل المحفز لا يكاد يذكر.

الهدف من عملنا هو إجراء دراسة نظرية شاملة حول التكسير الهيدروجيني، باستخدام بقايا عمود التقطير. ونحن نهدف إلى التحقق من صحة النتائج التي توصلنا إليها عن طريق إجراء محاكاة باستخدام برنامج هايسيس.

الأهداف المحددة لعملنا هي كما يلي

- اقتراح تنفيذ وحدة التكسير الهيدروجيني في مصفاة حاسي مسعود.
- استخدم بقايا عمود التقطير للحصول على منتجات أخف.
- زيادة كمية المنتجات الأخف التي تم الحصول عليها.
- تحقيق منتجات عالية الجودة بشكل انتقائي مع تقليل التكاليف.

- إنشاء وحدة تكسير هيدروجيني فعالة من حيث التكلفة تنتج منتجات مرغوب

الكلمات المفتاحية: التقطير الجوي , التكسير الهيدروجيني , التكسير التحفيزي , مواد بترولية محاكاة الهايسس

Résumé

En industrie pétrolière, les procédés clés comprennent la séparation, la transformation, l'amélioration et la purification. Ces procédés sont essentiels pour obtenir des produits de haute qualité qui répondent aux exigences d'utilisation humaine, de transport et environnementales. Parmi les procédés de séparation, le craquage catalytique est utilisé pour convertir les hydrocarbures en composés de poids moléculaire plus faible.

Lorsque du gaz d'hydrogène est injecté pendant le craquage catalytique, le procédé devient de l'hydrocraquage, qui présente plusieurs avantages par rapport au craquage catalytique traditionnel. L'hydrogène assure une expansion rapide, augmente l'activité catalytique et permet de travailler à des températures plus basses et de manière plus sélective. De plus, grâce à l'hydrogène, le dépôt de coke et la désactivation du catalyseur sont négligeables.

L'objectif de notre travail est de réaliser une étude approfondie théorique sur l'hydrocraquage, en utilisant le résidu atmosphérique de la colonne de distillation comme matière première. Nous souhaitons valoriser nos résultats en effectuant une simulation à l'aide du logiciel HYSYS.

Les objectifs spécifiques de notre travail sont les suivants :

- Proposer la mise en place d'une unité d'hydrocraquage dans la raffinerie de HASSI MESSAOUD.
- Tirer parti du résidu atmosphérique de la colonne de distillation pour obtenir des produits plus légers.
- Augmenter la quantité de produits légers obtenus.
- Obtenir des produits de haute qualité de manière sélective, tout en réduisant les coûts.
- Réaliser une unité d'hydrocraquage efficace en termes de coûts et de production de produits favorables.

Mots Clés :

Distillation atmosphérique, hydrocraquage , craquage catalytique , produits pétroliers , HYSYS, simulation.

List of abbreviations

- H2: dihydrogen gas

- Ni: the chemical element nickel

- Mo: the chemical element molybdenum

- iso/n: the number of isoparaffin divided by the number of normal paraffin .

- H2S: sulfuric dihydrogen

- LPG: liquefied petroleum gas

- A P I: the degree of density according to American Petroleum Institute

- D24: the calculation of the density in a temperature of 24 ° C.

- A.S. T. M distillation: the distillation values according to the American

  company for testing materials.

- TBP : True boiling Point

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Chapiter II: Presentation of the Hassi Massoud RHM02 refinery

Chapiter III: Hydrocracking process

General introduction :

Oil is a natural resource of great importance all over the world and is used in many economic sectors and industries. Crude oil is extracted from the ground through exploration and drilling processes and then processed to produce various high-value petroleum products, such as fuels, chemicals, plastics, medicines, etc. The advanced technology and huge investments required to produce these products make it a vital industry in many countries, with a significant impact on people's daily lives.

The petrochemical industry in Algeria is one of the most important economic sectors, and is supported by the Algerian government as well as national and international companies. The Hassi Messaoud region, where many factories and petrochemical production facilities are located, is one of the most important production regions in Algeria. Petroleum products are mainly used as transportation fuels, but they also have many other uses in various industries.

Algeria plays a major role in the oil and gas industry, as it owns many refineries and oil ports, including the Hassi Messaoud refinery, which is one of the largest refineries in Algeria and the region. This refinery is characterized by the latest technologies and specialized processes that convert crude oil into high-quality petroleum products that meet international standards and provide fuel and commodities to the local and international markets.

The petrochemical industry is a highly competitive sector where profitability is of paramount importance. To remain competitive, this industry must constantly adapt to significant technological developments in increasingly complex refineries. Thus, better knowledge of markets, cost formation mechanisms and optimization tools is essential, as well as control of operations, their performance, flexibility of use and possibility of exploitation, as well as a good component. Knowledge of products, their characteristics and implementation limitations to ensure safety and environmental preservation.

In the refining complex, the atmospheric distillation unit (topping) is of crucial importance for operation, since fractionation of the ore makes it possible to produce not only finished products that can be directly recycled in the domestic and international markets, but also semi-finished products necessary for the operation of other units such as refinement Catalyst, extraction of aromatics or production of liquefied gases. This unit includes a series of basic equipment for its

operation such as exchangers, furnaces and columns. The process improvement is to operate this equipment under optimum performance and safety conditions for

The content of the thesis is divided into four chapters:

-In Chapter I : General information on separation processes and Refining

-In Chapter II : Presentation of the Hassi Massoud RHM02 refinery

-In Chapter III: the Hydrocracking process

-In Chapter IV: Simulation of Hydrocracking Unit using Aspen HYSYS

-In the end, the general Conclusion

Chapter I: General information on separation processes and Refining

I.1 The Refining:

Refining, also known as petroleum refining or oil refining, refers to the industrial process of transforming crude oil into various valuable products through a series of physical and chemical processes. Crude oil is a complex mixture of hydrocarbons, impurities, and other compounds extracted from underground reservoirs. The primary objective of refining is to separate, convert, and upgrade these hydrocarbon compounds into useful products such as gasoline, diesel, jet fuel, heating oil, lubricants, asphalt, and petrochemical feedstocks.

Refining involves several key processes, including distillation, cracking, reforming, hydrotreating, and blending. Distillation is a primary separation method used to separate crude oil into different fractions based on their boiling points. Cracking processes break down heavy hydrocarbon molecules into lighter, more valuable products. Reforming processes modify the molecular structure of hydrocarbons to enhance their octane rating and improve their performance as fuel. Hydrotreating processes remove impurities and contaminants, such as sulfur, nitrogen, and metals, to meet product quality and environmental specifications. Blending involves mixing different fractions and additives to achieve desired product specifications and performance characteristics.

Refining plays a crucial role in the energy industry, as refineries produce the fuels and other petroleum-based products that meet the demands of transportation, industry, and everyday life. It requires advanced technologies, skilled personnel, and adherence to stringent safety, environmental, and quality standards to ensure the production of high-quality, compliant products.

Overall, refining is a complex and essential process that converts crude oil into a range of valuable products that power our vehicles, heat our homes, and provide raw materials for various industries.

I.1.1 Overview of Petroleum Refining:

Petroleum refining is a crucial industrial process that transforms crude oil into various valuable products. It involves a series of physical and chemical processes aimed at separating, converting, and upgrading hydrocarbon compounds present in crude oil. The primary objective of refining is

to produce high-quality fuels, such as gasoline, diesel, and jet fuel, along with other products like liquefied petroleum gas (LPG), asphalt, lubricants, and petrochemical feedstocks.

Refineries play a vital role in the energy industry by meeting the demand for transportation fuels and other petroleum-based products. They serve as complex processing facilities with multiple refining units, each designed to perform specific tasks. Common process units include distillation units for separating crude oil into different fractions, catalytic converters for converting heavy hydrocarbons into lighter ones, cracking units for breaking down large hydrocarbon molecules, and hydrotreating units for removing impurities and improving product quality.

Refinery configuration can vary based on factors such as feedstock characteristics, market demand, and desired product slate. Different refinery configurations include topping refineries, which focus on distillation and produce mainly gasoline and fuel oil, and complex refineries, which have additional units for secondary processing and produce a broader range of products.

To ensure high-quality products and comply with environmental regulations, refineries employ various pre-treatment processes. These include desalting to remove salt and water, desulfurization to reduce sulfur content, and other treatments to remove impurities like phosphorous, nitrogen, and metals.

I.1.2the Role of Refineries in the Energy Industry

Refineries play a crucial role in the energy industry by transforming crude oil into a range of useful products. These products include transportation fuels such as gasoline, diesel, and jet fuel, as well as heating oil, lubricants, and feedstocks for the petrochemical industry. Refineries also produce asphalt, which is used in the construction industry for roads, roofs, and other applications.

The products produced by refineries are essential to the functioning of modern society. Transportation fuels power vehicles, airplanes, and ships, enabling commerce and transportation of people and goods. Heating oil is used to heat homes and buildings, especially in colder climates. Lubricants are used to reduce friction and wear in machinery and engines, extending their lifespan and improving efficiency. Petrochemical feedstocks are used to produce a range of materials, including plastics, synthetic fibers, and chemicals.

Refineries also play a significant role in the economy. They provide employment opportunities, contribute to government revenue through taxes and royalties, and support related industries such as transportation, construction, and manufacturing.

However, refineries also face challenges related to environmental and safety concerns. The production of petroleum products can generate emissions and waste, which can have negative impacts on air and water quality. Refineries are subject to strict regulations and monitoring to ensure compliance with environmental and safety standards.

I.1.3 Historic overview:

The first refineries used horizontal, elevated tanks to heat the crude oil and vaporize its volatile components. The hot vapor would rise, cool, and condense in a batch operation. The process was repeated at different temperatures to separate the various fractions. The technology was simple, refineries were easy to set up, and before long, refining capacity exceeded crude supply. The need for improved product separation led to the use of fractionating columns, which allowed the different boiling-point cuts to be separated out in a continuous process. John D. Rockefeller sought to consolidate the U.S. refining business, and in 1870 he established the Standard Oil Co. with his partners . By 1879, Standard Oil controlled 90% of the U.S. refining capacity . The number of automobiles and the demand for gasoline greatly increased following the advent of mass production. Distillation processes, however, could only produce a certain amount of gasoline depending on the composition of the crude oil, and so scientists and engineers searched for new ways to increase the yield and performance of gasoline. Thermal cracking processes were first discovered in 1913, when heat and pressure was used to break down, rearrange, and combine hydrocarbon molecules .

 The introduction of catalytic cracking and polymerization processes in the mid- to late 1930s met the demand for higher octane gasoline. Eugene Houdry developed the first commercial process of cracking in the presence of clay mineral catalysts, which resulted in the large hydrocarbon molecules breaking apart; the products were converted to branched paraffins, naphthenes, and aromatics with desirable properties . Visbreaking, another form of thermal cracking, was developed in the late 1930s to produce a more desirable and valuable product slate. In the 1940s, alkylation processes were developed to create high-quality aviation fuels for the war effort, which later were used extensively to produce gasoline blending stocks.

I.2 Physical separation processes:

Separation processes are used in the oil and gas industry to separate the different constituents of a mixture of hydrocarbons. These processes use different separating agents such as heat, solvents, solids (adsorbents) and cold. They make it possible to separate the constituents without modifying their chemical structure so that the sum of the constituents at the outlet is equal to that of the initial mixture.

A physical separation process comprises four steps: the preparation of the charge, the contact of the two phases, the separation of the two phases and the recovery of the separating agent (heat or solvent) to optimize the industrial process.

I.2.1. Distillation:

I.2.1.1 Introduction:

Distillation is a process of physical separation which consists in splitting a liquid mixture into several pure constituents, by exploiting the difference in boiling temperature between them. It is the most widely used separation process in the oil and gas industry for the production of refined products such as gasoline, diesel, kerosene, and fuel oil. Distillation is based on the principle of vaporization and condensation of different chemical species at specific temperatures. The distillation column is the main equipment used for this process, and is designed to allow a series of elementary contacts between the liquid and vapor phases to obtain an efficient separation of the different components. Distillation is also used in other industrial sectors, such as the production of alcohol, perfumes, and pharmaceuticals.

I.2.1.2 Operation of a distillation column:

Industrial distillation columns operate continuously, permanently fed by a feed whose composition, flow rate and temperature are constant. They produce a distillate at the top and at the bottom a residue whose composition, flow rate and temperature are also constant. The pressure varies slightly between top and bottom due to pressure drop across the plateaus, but to a first approximation the pressure is constant.

The operation of a distillation column with plates can be described according to the flows of the load and the products circulating in the column. The feed is preheated and introduced into the flash zone of the column corresponding to a vaporized percentage determined according to the

composition of the feed. The distillate is partly recovered as reflux above the first plate of the column, while the liquid contained in the flask is sent to storage after cooling or to another unit for complementary operations. The column bottoms liquid is partly reheated in a reboiler and then reintroduced into the column below the last plate, the other part constituting the residue.

Reflux is an internal liquid flow introduced at the head of the column at a well-defined flow rate and temperature. It descends from plate to plate and establishes the partial heat balances on each plate and the temperature gradient in the column. Reboiling allows the revaporization of the light fraction contained in the bottom liquid of the column. It can be carried out by reboiling or stripping depending on the composition of the products to be treated. The internal circulation of the column is carried out in the trays of the column, which ensure the intimate contact between the liquid and the vapor. The quality of the separation is directly related to the number of trays in the column.

I.2.1.3 Initial crude distillation:

Initial crude distillation is a separation process that involves heating crude oil in a distillation column to separate its components based on their boiling point. The different components of crude oil have different boiling points, allowing them to be separated into fractions that have specific uses.

The distillation process starts by feeding the crude to the lower part of the distillation column. The crude is heated, usually by burning natural gas, heavy fuel oil or other fuels, which vaporizes the components of the crude. The vapors rise in the distillation column and are gradually cooled by plates or tube bundle columns. The crude components condense at different levels depending on their boiling point, thus forming fractions.

The lighter fraction, called naphtha, is typically used as a feedstock for the production of fuel and petrochemicals such as plastics. The middle fraction, called kerosene, is used as fuel for airplanes and for home heating. The heaviest fraction, called gas oil or diesel, is used as fuel for trucks and cars. The heaviest fraction, called residue, is used to produce lubricants and bitumens.

Initial crude distillation is the first process for refining crude oil and is used to produce the various fractions which are then processed in other refining processes to obtain end products such as gasoline, diesel and kerosene.

I.3 Heavy crude oil refining:

The processing of heavy oils in refineries, especially in the existing refineries, presents many difficulties due to their unfavorable characteristics. Due to very low H/C ratios, the yields of straight-run gasoline, kerosene, and diesel are very poor due to high levels of heavier components such as asphaltenes. A major fraction of the heavy crude oil after fractionation in an atmospheric distillation column is expected to report to the residue stream as the feed to the vacuum distillation unit.

The economic value of the residue stream is very low, and therefore, conversion techniques are required to upgrade them to maximize the production of valueadded streams. The upgrading of the residue streams is generally done in one of the two methods, namely, hydrogen addition (e.g., hydrotreating or hydrocracking) or carbon rejection.

Chapter II: Presentation of the Hassi Massoud RHM02 refinery

II.1. introduction:

The new refinery located four kilometers southeast of the town of Hassi-Messaoud, it processes 1,100,000t/year of crude from the processing unit to transform it into commercial finished products: diesel, kerosene, normal gasoline, premium gasoline .

II.2. Construction of the refinery (RHM02):

The RHM2 study was carried out in 1976 and entrusted to ALTEC (Algerian Engineering Company) and H.E France (Hydrocarbon Engineering). The assembly was carried out by ENGTP (formerly ALTRA). The RHM2 is designed and studied to process crude oil from Hassi-Messaoud Sud with an annual processing capacity of 1,070,000 t/year.

Atmospheric distillation was commissioned in May 1979, followed by catalytic reforming in October 1979. The design processing capacity is 100,000 t/year for reformate, 412,000 t/year for gas oil, 40,500 t /year for the Jet A1, 42,000 t/year for normal gasoline and 42,000 t/year for premium gasoline.

II.3. Description of the production units of the Hassi Massoud refinery (RHM02):

It is made up of four units:

-U 200: Atmospheric distillation

-U 300: Pre-treatment of naphtha (Hydrodesulphurization)

-U 800: Catalytic Reforming

-U 900: Storage, shipping pumps and utilities
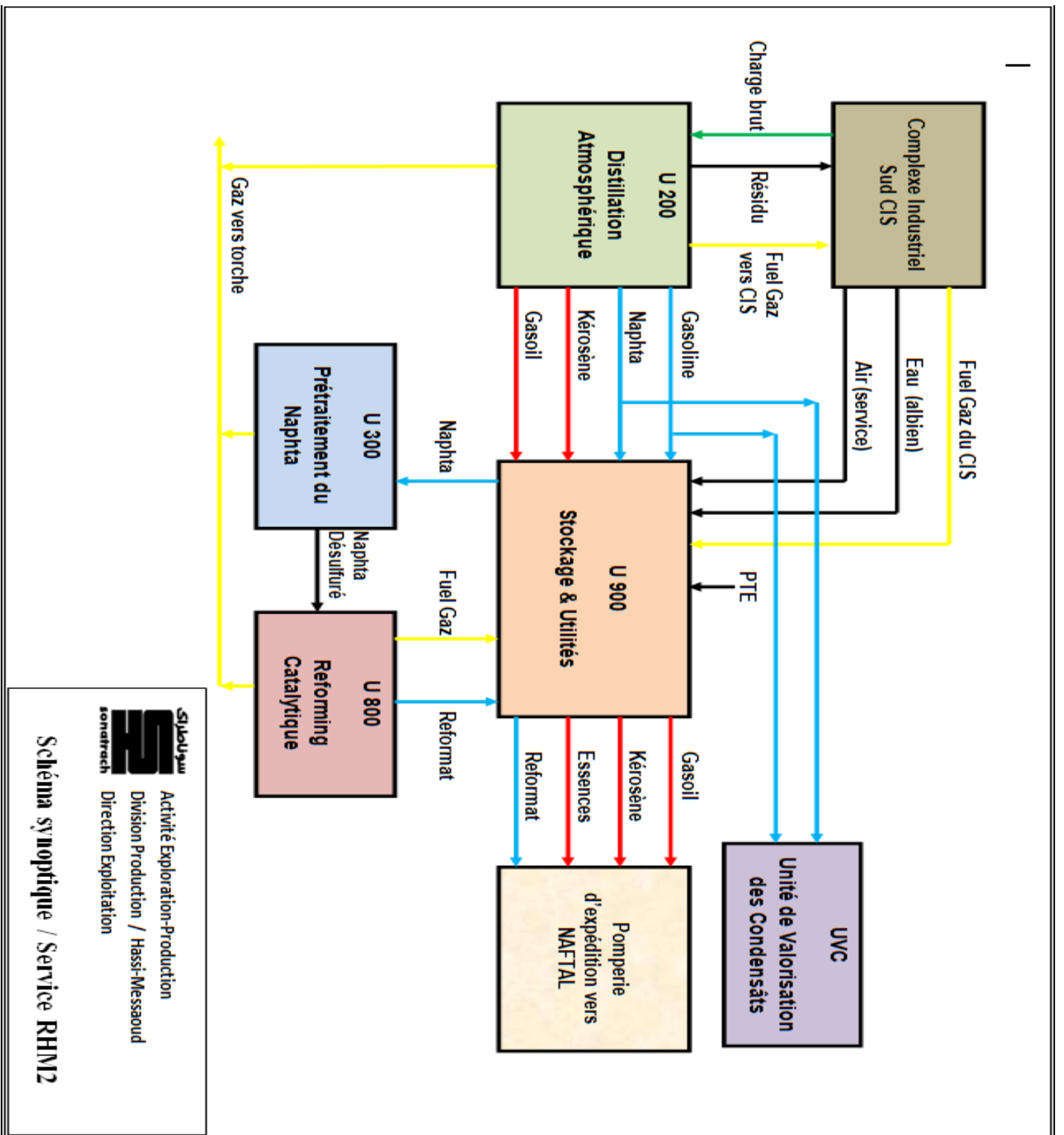
Figure II.1: Synoptic diagram of the RHM2 Refinery

II.3.1. Atmospheric distillation units (U200):

The crude load from the shipping pump station of the treatment department at a pressure of 3.5 bars is taken up by a pump upstream of which it is injected with ~5% volume of water previously preheated in an exchanger and ~5 ppm volume of demulsifier relative to the volume flow rate of the crude feed.

The mixture is preheated to ~70°C in 02 exchangers in parallel; then brought into the electric field of the desalter.

The desalted crude is taken up by a pump, preheated in a series of exchangers at ~170°C; then heated to 330°C in the oven to enter the expansion zone of the atmospheric distillation column; this column is equipped with 29 clamshell trays, the latter are distributed in 02 zones:

- 1st expansion zone 03 trays
- 2nd splitting zone 26 trays

The vaporized part leaves the top of the expansion zone at □220°C to feed the fractionation zone at the 21st plate of the DA201 column.

The products withdrawn are: Residue or reduced crude, Diesel oil, Circulating Reflux, Kerosene, Naphtha, Gasoline + gas

•**The residue** is withdrawn at ~325°C from the bottom of the column (expansion zone); is sent to slope after giving up its colors to the preheating of kerosene and the crude load in a battery of exchangers; then cooled in a battery of air-humidified air coolers to be mixed with the crude in the treatment department.

•**The gas oil** is withdrawn at ~325°C from the bottom of the fractionation column; one part is reheated to ~350°C in another furnace to eliminate the light fractions and maintain the temperature gradient in the fractionation column and the other part is sent to storage after having given up its calories to the crude charge in an exchanger; then cooled in a battery of dry air coolers.

•**The circulating reflux** is withdrawn at ~230°C from the 16th plate of the fractionation column; part is sent through two reboilers to yield its calories to the reboiling of naphtha and gasoline.

The return from the reboilers and the other part of the circulating reflux return to the 13th tray of the fractionation column after having given up its calories to the crude feed in an exchanger then cooled to ~110°C in a battery of air coolers at dry air.

•**The kerosene** is withdrawn at ~200°C from the 12th tray of the fractionation column, it flows by gravity into a small column (Stripper) of 06 trays.

Reboiling of the bottom of Stripper is done in the reboiler at ~240°C by the residue for elimination of the light fractions (adjustment of the flash point), the overhead vapors of this column return to the 11th plate of the fractionation column .

The kerosene, leaving the stripper, is cooled in a humidified air cooler after having transferred its calories to the crude load in the exchanger; a part is sent to the electrostatic precipitator for elimination of traces of water and undergo treatment with soda to adjust the acidity; before being sent to storage, it is injected with an antistatic product (STADIS 450) to adjust the electrical conductivity and the other part is mixed with diesel.

•**The naphtha** is withdrawn at ~160°C from the 6th plate of the fractionation column, it flows by gravity into a small column (Stripper) of 06 valve plates.

Stripper bottom reboiling is done by reflux circulating in the reboiler at ≈170°C to eliminate the light fractions (setting of the initial point), the overhead vapors of this column return to the 5th plate of the fractionation column.

The naphtha, leaving the stripper, is cooled in a humidified air air cooler after having transferred its calories to the crude load in the exchanger then; sent to storage to serve as feed to the naphtha pretreatment and reforming section.

The overhead vapors DA 201 from the fractionation column at a temperature of 90° C. are cooled in a battery of dry air coolers; then condensed and separated in the flask; the gaseous phase (rich in C3 - C4) is sent to the treatment department towards the 3rd stage recovery unit.

Part of the liquid phase (condensate) is sent to the fractionation column as overhead reflux and the other part is sent to a stabilization column with 26 valve trays.

Reboiling at the bottom of the stabilization column is done by reflux circulating in the reboiler at ~120°C to adjust the TVR (0.700 to 0.900 bars) of the gasoline. The stabilized gasoline is sent to

storage after having transferred its calories to the charge of the stabilization column in the exchanger; then cooled in a humidified air air cooler to be used for the preparation of essences.

The DA 203 overhead vapors from the stabilization column are cooled in a battery of dry air coolers then; condensed and separated in a flask; the gaseous phase (rich in C3-C4) is in the treatment department towards the 3rd stage recovery unit and the liquid phase is sent as reflux from the head of the stabilization column.

II.3.2 U300: Naphtha pre-treatment section:

The annual capacity of the naphtha pre-treatment section (design) is: 100,022 tonnes.

The purpose of pre-treatment is to eliminate the main poisons contained in the charge (such as: sulphur, nitrogen compounds, oxygen, arsenic, etc.) and therefore to extend the life of the reforming catalyst

The charge from a naphtha tank is mixed with a flow ($\leq$ 1000 Nm3/h) of hydrogen.

This mixture (Naphtha+H2) is preheated in a battery of exchangers by the effluent leaving the reactor at ~230°C, then heated in an oven at ~320°C (t° required for the desulfurization reaction) before entering in the catalytic reactor. The reactor outlet effluent is cooled to approximately 40°C in a battery of humidified air air coolers after having transferred its calories to the load in a series of exchangers, then flashed in the separator drum; the gaseous phase is sent to the flare or fuel gas.

The liquid phase is stripped in a column of 28 valve plates after being preheated to ~95°C in the exchanger by the effluent leaving the K301 reactor.

The bottom of the column is reheated to ~220°C in the furnace to serve as a charge for the reforming.

The vapors at the top of the column are cooled in a battery of air coolers with humidified air then condensed and separated in a flask; the gaseous phase is sent to fuel-gas and the liquid phase is sent as column head reflux.

Figure II. 2 :Topping unit diagram

II.3.3 U 800: Catalytic reforming section:

The annual production capacity of the reforming section (design) is: 100,000 tonnes of reformate.

The goal of catalytic reforming is to transform low octane number hydrocarbons into high octane number hydrocarbons (86 to 92).

The desulfurized charge is mixed with (~25.103 Nm3) of hydrogen.

The mixture that constitutes the reactor charge is preheated in a series of heat exchangers by heat exchange to ~390°C with the reactor effluents, then heated in the first furnace to ~500°C before entering the first reactor, then the same successive cycle. This process being endothermic, this is why it is necessary to heat the mixture during the reaction to maintain a sufficient temperature level in the reactors.

At the outlet of the last reactor, the effluents are first cooled to ~346°C in the exchanger to transfer their calories to the reactor load. Part of the effluent is used for reboiling the bottom of the column in the reboiler at ~210°C for adjusting the TVR of the reformate (0.300 to 0.550 bars).

The mixed effluents are cooled to ~160°C in a battery of exchangers to transfer their calories to the load, then cooled in a battery of humidified air air coolers before being flashed in a vertical separator drum. The hydrogen-rich (~80%) gas phase is mixed with the charge at the discharge of the charge pump and the other part is sent to the pre-treatment to be mixed with the naphtha charge.

The liquid phase (unstabilized reformate) which constitutes the load of the stabilization column is preheated to ~150°C in a battery of exchangers through the bottom of the column, stabilized in a column of 29 valve plates, then sent to the storage after cooling in a humidified air air cooler to be used for the preparation of essences.

Reboiling at the bottom of the reformate stabilization column is done by part of the effluents leaving the reactors in a reboiler at ~210°C to adjust the vapor pressure of the reformate.

The overhead vapors from the stabilization column are cooled in a battery of humidified air cooling towers then condensed and separated in a drum; the gaseous phase is sent to fuel gas or to a flare. The liquid phase, one part is sent as overhead reflux and the other part is sent to the CIS (3rd stage) or to the torch.

Figure II. 3 :Reforming unit diagram

II.3.4 U 900: Storage, shipping pumps and utilities :

Sixteen (16) is the number of tanks installed to satisfy this operation. This is only the storage of refinery products, the crude feedstock comes directly from the center (CIS) without being stored.

II.3.4 U 900: Storage, shipping pumps and utilities:

Table II.1**:** Storage pack

N°	Bac (RS)	Volume (m^3)	Roof	content
1	903	2520	Floating	Reformat
2	904	2520	Floating	Gasoline
3	905	2520	Floating	Naphtha
4	906	2520	Floating	Reformat
5	907	2520	Floating	Reformat
6	908	2520	Floating	Reformat
7	909	2520	Floating	Ess.Nor
8	910	2520	Floating	Ess.Nor
9	911	2520	Floating	Reformat
10	912	2520	Floating	Ess.Super
11	913	2520	Floating	Kerosene
12	914	2520	Floating	Kerosene
13	915	16620	Fixed	Gas-oil
14	916	16620	Fixed	Gas-oil
15	917	16620	Fixed	Gas-oil
16	918	2520	Floating	Kerosene

Chapter III: the Hydrocracking process

III.1. General:

Hydrocracking is a process of converting heavy hydrocarbons into lighter and more valuable compounds, used in particular for vacuum distillates and deasphalted residues. It makes it possible to produce different gasolines, jet fuel and diesel, as well as lubricating bases for engine oils. The process was first implemented in 1927 in Germany and became common in the United States from 1959. Hydrocracking can also be combined with catalytic cracking in some countries to produce middle distillates and fuel more efficiently.

III.1.1: General characteristics of hydrocracking reactions:

Hydrocracking reactions are essentially characterized by the breaking of a C-C bond. depending on the position of the C-C bond attacked, three main types can be distinguished

1) Simple hydrocracking reactions: C-C attack in a chain

$$R\text{-}CH_2\text{-}CH_2\text{-}R' + H_2 \longrightarrow R\text{-}CH_3 + R'\text{-}CH_3$$

2) Hydrodealkylation reaction: attack of C-C adjacent to a nucleus.
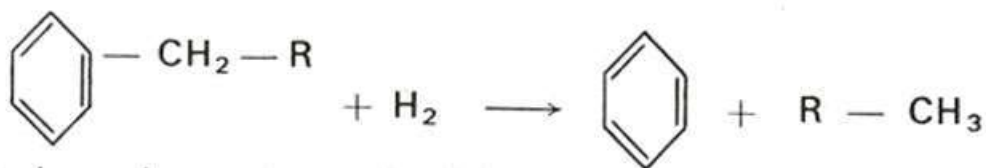
3) Ring opening reaction: C-C attack in a ring.

A) Thermodynamic considerations:

Hydrocracking reactions are exothermic and do not change volume. Under hydrogen pressure, these reactions are almost complete below 500°C. Saturation reactions of olefins are also complete,

but those of aromatics are balanced. The exothermicity (Table III.1) varies depending on the reactions, but it is around 12 kcal/mol or 0.55 kcal per normal liter of H2 consumed. Parallel saturation reactions are much more strongly exothermic and increase the overall exothermicity of hydrocracking processes.

Table III. 1: comparison of the results obtained with acid and non-acid catalysts

TYPE DE RÉACTIONS		CHALEUR DE RÉACTION MOYENNE (400°C)	
		kcal/mole	kcal/l N d'H₂
A - HYDROCRAQUAGE			
Paraffines :	$RH + H_2 \longrightarrow R'H + R''H$	11 à 14	0.49 à 0,625
Naphtènes :	$R\_\bigcirc + H_2 \longrightarrow R'H$	10 à 12	0.45 à 0.54
Aromatiques :	$R\_\hexagon + H_2 \longrightarrow RH + \hexagon$	10 à 11	0.45 à 0,49
B - SATURATION			
Oléfines :	$C_n H_{2n} + H_2 \longrightarrow C_n H_{2n+2}$	27 à 31	1,2 à 1,4
Aromatiques :	$R\_\hexagon + 3 H_2 \longrightarrow R\_\bigcirc$	48 à 52	0,71 à 0,77

III.1.2. Mechanism of the reaction:

The hydrocracking reaction is an exothermic reaction without volume change, which can be considered practically complete under hydrogen pressure. The saturation reactions of the olefins are also balanced, but those of the aromatics are balanced. Saturation parallel reactions are highly exothermic and increase the overall exothermicity of the hydrocracking process.

Studies indicate that the hydrocracking reaction is mediated by coronium ions and that the reaction products are isomerized into branched chains. The C-C bond cleavage reaction is preceded by a rapid isomerization reaction following a mechanism analogous to that of catalytic cracking.

III.2. Catalytic hydrocracking:

Catalytic hydrocracking is a catalytic cracking reaction with a hydrogenation overlay. The products obtained are similar to those obtained in catalytic cracking. The light products are mainly in C4/C5 and the iso/n ratio is higher in hydrocracking. Aromatic hydrocarbons are preferentially dealkylated by breaking the C-C bond adjacent to the ring and ring opening only occurs after saturation. The reaction temperature affects the product distribution by increasing the C3/C4 ratio and the aromatics content while decreasing the iso/n ratio.

Tables III.2 and III.3 bring together data on the hydrocracking of a certain number of pure products

Table III. 2: distribution of paraffin hydrocracking products

	iso-Butane	n-Butane	n-Hexane	n-Heptane	2-2-3-Tri-méthyl-butane	n-Octane	2-2-4-Tri-méthyl-pentane	n-Décane	iso-Do-décane	n-Do-décane	n-Tétra-décane	n-Hexa-décane
Catalyseur N°	11	11	9	9	9	9	9	9	9	9	9	9
Charge, moles/l.h	15	15	7,0	7,0	7,2	7,1	7,2	7,1	7,2	7,1	7,1	6,9
V/H/V	1,56	1,56	0,91	1,02	1,04	1,16	1,19	1,38	1,62	1,62	1,85	2,0
Temps de contact en s	54	52	64	62	66	63	64	64	63	63	64	65
Sévérité : % poids	—	—	4	55	39	77	86	95,5	53	97	98,7	98,5
Produits : % poids charge												
CH_4	—	—	1,8	0,1	0,5	—	0,9	—	—	2,1	0,3	—
C_2H_4	—	—	—	—	—	—	—	—	—	—	—	Trace
C_2H_6	—	—	—	—	—	Trace	0,1	0,6	Trace	0,5	0,1	Trace
C_3H_6	—	—	—	—	—	—	—	—	—	0,1	0,6	0,1
C_3H_8	0,1	—	Trace	23,2	12,9	13,4	2,7	12,1	3,3	10,9	11,8	8,7
C_4H_8	—	—	} 2,0	0,1	0,1	0,1	0,3	0,1	0,2	0,1	0,1	—
$n\text{-}C_4H_{10}$	0,2	96,0	} 2,0	5,6	3,6	16,5	3,9	9,4	3,8	10,5	10,3	10,2
$iso\text{-}C_4H_{10}$	99,2	4,0	}	22,2	16,1	23,7	71,4	20,1	23,7	23,6	24,2	22,7
C_5H_{10}	—	—	—	} 3,2	} 2,7	0,1	—	0,1	Trace	0,1	—	—
$n\text{-}C_5H_{12}$	0,5	—	—	} 3,2	} 2,7	4,4	1,3	5,5	1,7	3,8	5,9	3,8
$iso\text{-}C_5H_{12}$	—	—	—	}	}	16,4	2,8	21,8	6,6	16,9	18,7	20,2
C_6H_{12}	—	—	} 96,0	—	—	—	—	Trace	Trace	Trace	0,1	0,1
C_6H_{14}	—	—	} 96,0	0,5	2,8	1,5	0,9	22,8	5,9	17,2	19,2	18,0
C_7H_{14}	—	—	—	0,5	—	—	—	—	Trace	Trace	Trace	—
C_7H_{16}	—	—	—	44,6	61,3	0,9	2,0	1,3	2,6	6,1	4,8	6,1
C_8H_{16}	—	—	—	—	—	0,1	Trace	—	0,1	Trace	—	0,1
C_8H_{18}	—	—	—	—	—	22,9	13,7	0,8	2,3	3,5	0,9	5,7
Oléfines $> C_8H_{16}$	—	—	—	—	—	—	—	Trace	0,2	Trace	Trace	0,1
Paraffines $> C_8H_{18}$	—	—	—	—	—	—	—	5,4	49,6	4,6	3,0	4,2

Table III. 3: distribution of hydrocracking products according to the nature of the charge

	PARAFFINES NORMALES			BICYCLIQUE SATURÉ		AROMATIQUES		
	n-HEXA-DÉCANE	n-HEXA-DÉCANE	n-OCTANE	DÉCALINE		TÉTRA-LINE	TÉTRA-LINE	n-BUTYL-BENZÉNE
CONDITIONS								
Pression (atm.)	67	35	34	68	68	68	68	68
Température (°C)	372	387	388	371	467	371	411	410
Vitesse spatiale V/H/V	0,94	0,93	1,00	0,94	0,97	0,93	0,96	0,96
Moles H_2/mole HC	24,5	24,7	12,9	12,0	11,8	9,7	9,4	10,8
PRODUITS : % poids de la charge								
C_1	0,00	0,16	0,20	0,00	0,59	0,00	0,12	0,12
C_2 Saturé	0,31	0,30	0,80	0,28	1,60	0,03	0,06	0,40
Oléfine	0,00	0,00	0,00	0,08	0,00	0,00	0,00	0,00
C_3 Saturé	14,67	12,48	10,36	3,54	9,45	0,61	0,33	4,74
Oléfine	0,03	0,43	0,13	0,37	0,54	0,02	0,02	0,32
C_4 Normal	9,43	8,67	9,85	3,59	5,80	0,45	0,41	14,69
Iso	29,39	30,87	17,08	21,06	17,70	1,62	0,58	9,02
Oléfine	0,02	0,34	0,39	0,32	0,44	0,06	0,03	0,27
C_5 Normal	3,20	2,98	2,54	0,51	1,06	0,00	0,00	0,08
Iso	21,42	19,38	9,16	8,15	7,94	0,51	0,36	2,00
Oléfine	0,07	0,14	0,10	0,05	0,23	0,03	0,02	0,03
Cyclopentane	...	...	...	0,54	0,72	...	...	0,03
C_6 Normal	1,64	0,95	0,24	0,44	0,82	0,04	0,01	0,04
Iso :								
3-Méthylpentane	4,61	3,82	0,32	2,46	2,80	0,09	0,01	0,24
2-Méthylpentane	7,05	6,38	0,56	3,56	4,02	0,14	0,03	0,34
2-3-Diméthylbutane	1,60	1,74	...	0,76	0,90	0,03	...	0,07
2-2-Diméthylbutane	0,08	0,07	0,02	0,03	0,04	0,00	0,00	Trace
Méthylcyclopentane	< 0,35	< 0,13	< 0,03	20,98	11,18	0,55	0,33	1,39
Cyclohexane	0,00	0,00	0,00	1,40	0,98	0,08	0,01	0,11
Benzène	...	...	...	0,22	1,44	2,56	2,07	35,63
Toluène	...	...	...	1,48	4,64	1,52	1,83	12,23
C_7 Normal	0,57	0,60	0,05	...	...	...	...	...
1-cis-3-Diméthylcyclopentane Iso	2,44	3,36	0,14	...	...	...	...	...
Alkylaromatiques	0,68	1,45	...	...	...	...	...	...
Cycloparaffines (C_7+)	0,29	0,00	...	...	...	...	...	...
Bicycloparaffines	0,00	0,00	...	...	...	...	...	...
Alkanes (C_7+)	1,48	5,40	47,18	...	...	...	...	...
Non identifié	0,67	0,36	0,85	...	...	...	...	...
C_8 Aromatiques	...	...	...	1,86	5,78	0,85	0,68	5,43
C_9 Aromatiques	...	...	...	1,23	2,84	0,57	0,38	1,05
C_{10} Aromatiques (mono)	...	...	...	0,04	3,60	2,08	2,51	7,32
Cycloparaffines (C_7+)	...	...	...	22,96	10,32	...	...	2,16
Bicycloparaffines	...	...	...	1,76	4,57	1,04	0,58	0,72
Naphtalène	...	...	...	...	...	6,26	18,32	...
Tétraline	...	...	...	Trace	Trace	76,89	64,52	...
Non identifié	...	...	...	2,33	0,00	3,97	6,79	1,57
Rapport iso/normal :								
C_4	3,1	3,6	1,7	5,8	3,0	3,6	1,4	0,6
C_5	6,7	6,5	3,6	16,0	7,5	...	...	25,0
C_6	8,1	12,6	4,8	15,5	9,5	6,5	4,0	16,3
MCP/cyclohexane	...	...	...	15,0	11,4	6,9	33,0	12,6

The hydrocracking of C5/C6/C7 products on platinum-based catalysts on acid support shows that this catalyst does not act according to an identical mechanism, but that there is a significant intervention of non-acid catalytic hydrocracking. for these products. This is highlighted by the importance of demethanation and the relatively secondary role of the acidity of the support.

III.3. Characteristics of industrial processes:

The catalysts used in hydrocracking can be of two types: metal/acid support or oxides or sulphides/acid support. The supports commonly used are silico-aluminas, aluminas added with halogen or molecular sieves. The metals offered are noble metals such as platinum, or metals such as nickel or cobalt. The oxides or sulphides proposed are those of molybdenum, tungsten, nickel or cobalt. These catalysts can lead to demethanization reactions for C5/C6/C7 products. They are not very sensitive to poisoning by sulfur derivatives but are sensitive to nitrogen derivatives. Processes often have a first pretreatment step to remove basic nitrogen.

IV.3.1. One-step hydrocracking:

Hydrocracking plants consist of two main parts: the reaction section and the fractionation section. The reaction section can consist of one or two reactors, while the fractionation section can consist of several columns for stabilization, fractionation of liquid products, separation of C3-C4, etc. The products obtained depend on the operating conditions, the choice of the reaction system and the fractionation. The desired products are separated and the remaining fraction is recycled. Three companies currently license hydrocracking processes: Cal.Research and Universal OilProducts with the Isomax process, Union OilCompany of California with Unicracking, and H Oil (HydrocarbonisocrackinG and DevelopmentCompany) which is included in hydrotreating. Other companies such as Humble, Mobil, Shell, Gulf, Texaco and the Institut Français de Pétrole have also worked in this direction and are announcing the development of similar processes.

Diagram III.1 depicts a one-step processing unit. The fresh charge is mixed with the recycle gas and preheated before being introduced into the reactor where the catalyst is placed in a fixed bed. The effluent is then cooled and the recycle gas is separated in a high pressure separator. The final product is sent to the fractionation section. This diagram can be modified according to the needs, such as the points of injection of the recycle gas, the make-up gas and the recycle product. The one-step variant is often used to maximize middle distillates or for processing light products that are free of impurities that can poison the catalyst.
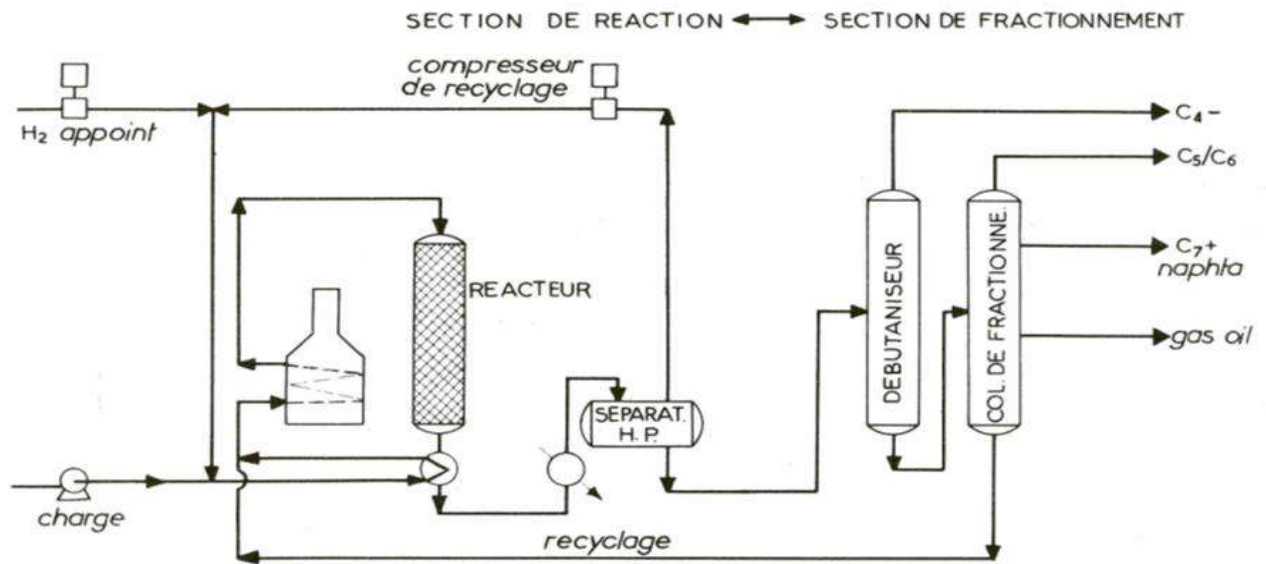
Figure III. 1: typical one-stage hydrocracking unit

III.3.2. Hydrocracking in two stages:

Diagram III.2 represents a two-stage hydrocracking unit with a common recycling circuit for the effluents of the two reactors, while diagram III.3 represents a two-stage unit with two different recycling circuits. In this last variant, the effluent from the reactor of the first stage is treated separately to avoid the presence of H2S in the second stage and in the fractionation columns. This modification makes it possible to use less noble materials in these sections, which leads to savings on investment. Two-stage hydrocracking processes allow maximum production of middle distillates, kerosene, carburetor or gasoline. In addition, two different catalysts are used in these two steps.
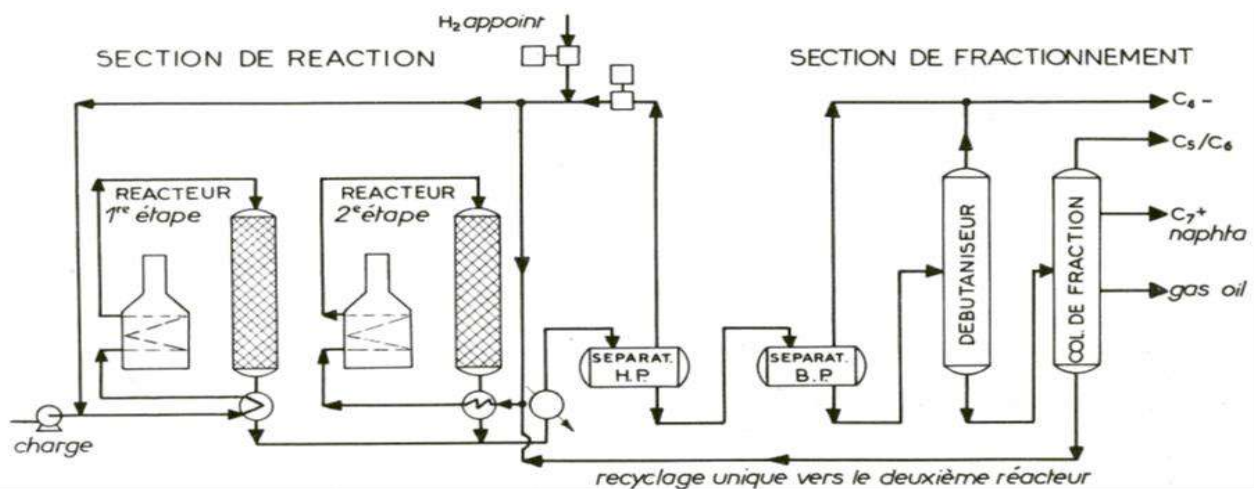

Figure III. 2: typical of a two-stage hydrocracking unit with a common recycle circuit
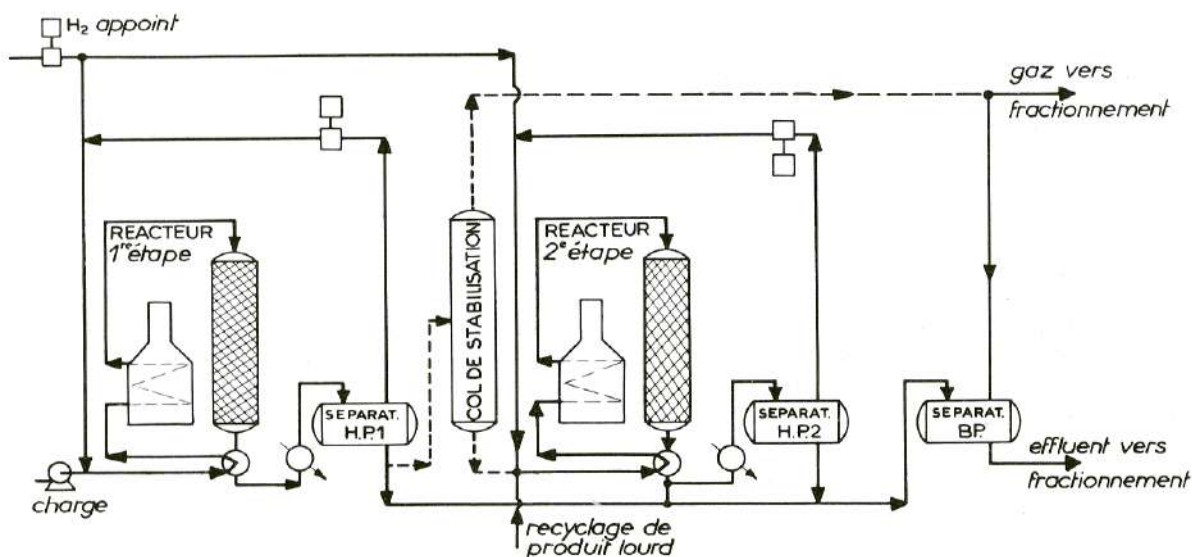
Figure III. 3: typical of a two-stage hydrocracking unit with a common recycling circuit

III.4. Hydrogen consumption:

The cost of hydrogen is an important aspect of these processes. Hydrogen consumption varies depending on the application, including hydrocracking of paraffins, naphthenes, olefins, aromatics, and decomposing sulfur, nitrogen, and oxygen compounds. In practice, calculating hydrogen consumption is only possible in some cases, such as hydrocracking naphthas for propane and butane production. Hydrocracking has the highest consumption and can be calculated based on the ratio of the average molecular weights of the feedstock and products. The the feedstock and the lighter the products, the higher the hydrogen consumption. The composition and sulfur content of the feedstock also affect hydrogen consumption. An example of the impact of feedstock on hydrogen consumption is presented in table III.4. which compares the hydrogen consumption in three different cases involving the treatment of feedstocks with different hydrocarbon compositions.

Table III. 4: The influence of feedstock nature on hydrogen consumption

CHARGE	GASOIL DE RECYCLAGE (CALIFORNIE)	GASOIL DE RECYCLAGE (ARABIE)	GASOIL (ARABIE)
Densité : °A.P.I.	31,9	31,2	35,2
Poids spécifique	0,866	0,870	0,849
Point d'aniline (°C)	68,5	82	90,5
Composition (volume %) :			
P	24	28	35
N	55	57	49
A	22	16	16
Distillation (A.S.T.M.)(°C) :			
P.I.	164	220	181
10 %	249	300	308
50 %	307	366	369
90 %	365	416	399
P.F.	411	452	427
PRODUITS			
Naphta (% volume) (82°C/160°C)	43,5	44,8	44,0
Carburéacteur (% volume) (160°C/260°C)	42,9	40,5	39,8
CONSOMMATION			
H$_2$, m³/m³ de charge	216	152	142

Based on data collected from the literature, the average consumption was estimated and presented in Table III.5.

Table III. 5: Average Hydrogen Consumption

charge	products	consumption
Heavy distillate (vacuum)	Medium distillate (max)	250 to 300
heavy distillate	Fuel (max)	300 to 500
Middle distillate	Jet fuel + gasoline	150 to350
Middle distillate	Gasoline (max)	250 to 350
Gasoline	$C_3 - C_4$	200 to 250

In these averages, the consumption will increase depending on the average aniline point and the content of aromatics, olefins, and sulfur

III.5. Integration of hydrocracking processes into refinery schemes:

The catalytic hydrocracking process is similar in principle to catalytic cracking, as both aim to convert heavy, low-value products into lighter, higher-volume products. However, catalytic cracking has limitations, particularly in terms of the characteristics of the gasoline produced and

the poor quality of the middle distillates obtained. Catalytic hydrocracking is more flexible and better adapted to the needs of modern refining. It can produce both high-octane gasoline and high-quality middle distillates. Different refinery schemes using catalytic hydrocracking have been described in the literature. Hydrocracking can replace catalytic cracking in schemes focused on producing maximum gasoline, or it can be a new method for producing high-quality middle distillates. Comparisons have been made between schemes using hydrocracking and catalytic reforming or other processes, showing that hydrocracking can produce a higher volume of gasoline from a vacuum distillate feed than other processes. Two typical refinery schemes using catalytic hydrocracking are presented in diagrams III.4 and III.5, and it is noted that in schemes focused on producing maximum gasoline, vacuum distillation can be replaced by viscosity reduction or coking units.
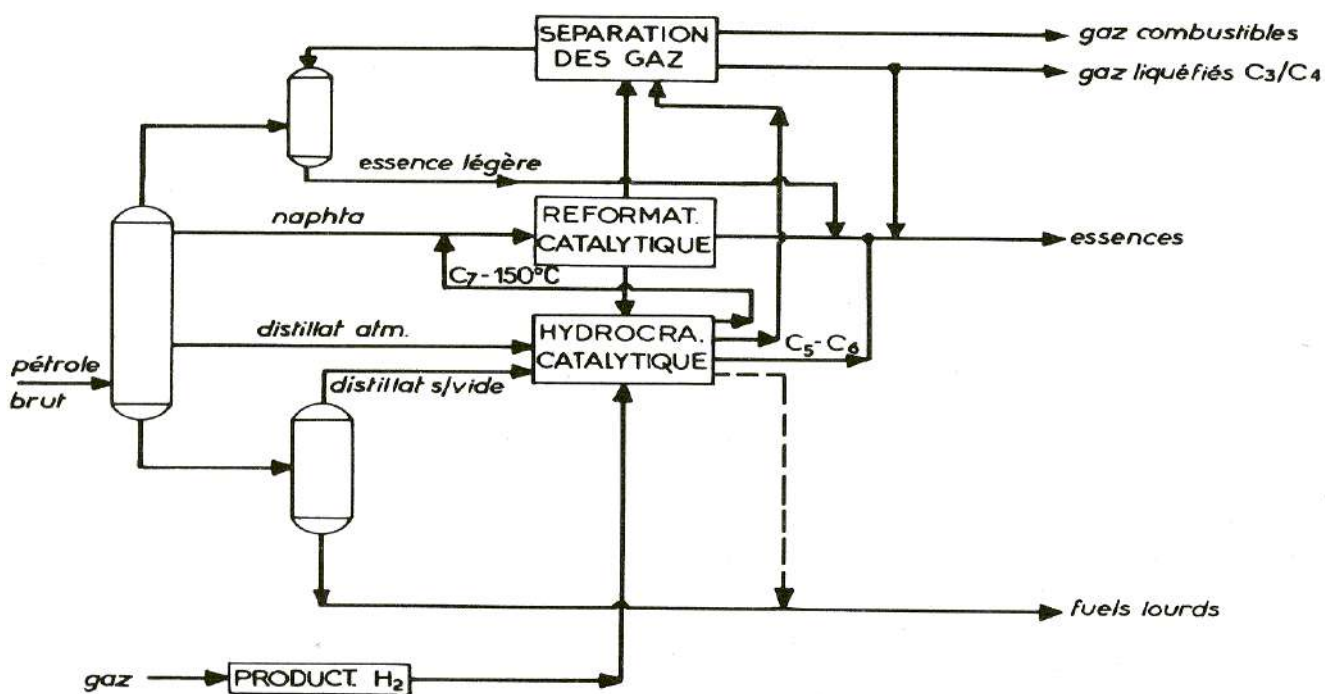

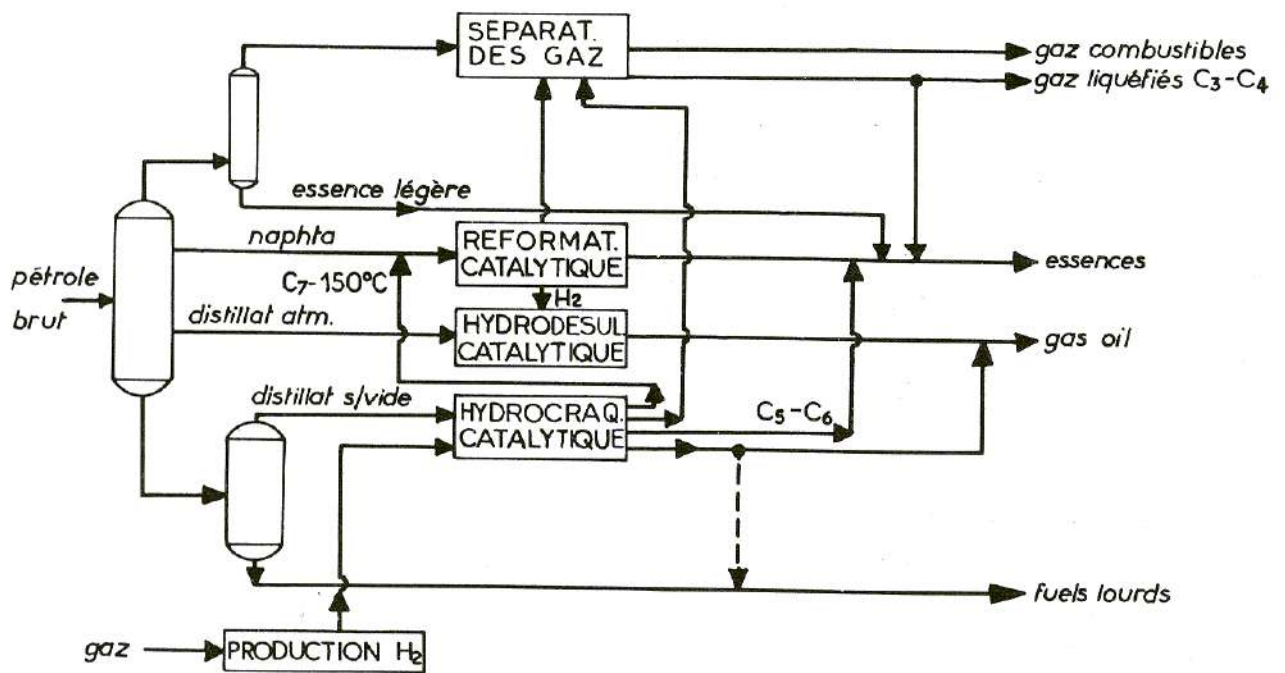Figure III. 4:shows integration for maximizing the production of gasoline

Figure III. 5:shows integration for maximizing the production of diesel.

III.5.1. Economics of hydrocracking processes:

III.5.1.1. Investments:

Investments vary depending on the severity of treatment, which depends on the feed (boiling point, unsaturation content) and the desired outcome (maximum gasoline or middle distillate production). It does not seem possible to make a valid comparison of investments according to the different processes. We have selected the average values for investments in a few typical cases (Table III.6). These investments are established based on the following: the boundary of the unit, hydrogen compression included, fractionation included (gas, light gasoline, reforming feed, light distillates).

Table III. 6: Investment estimate for hydrocracking unit (Capacity of 630,000 m3/year)

Charge	Products	Investments
Heavy distillate (vacuum)	Medium distillate (max)	6000000$
heavy distillate	Fuel(max)	7 to 9000000$
Middle distillate	Fuel(max)	4 to 9000000$

In addition to these investments, it should not be forgotten that the necessary hydrogen is rarely available in sufficient quantity and investments must be taken into account for the corresponding hydrogen production unit.

III.5.1.2. Operating costs:

Operating costs include utilities, catalyst consumption, labor, and maintenance costs.

III.5.1.2.1. Utilities consumption:

Utilities consumption varies depending on the severity of the operation (maximum gasoline or middle distillate production) and the nature of the feedstock.

In general, they are higher when the operation is more severe.

Since the reaction is highly exothermic, the supply of heat to the reaction section is reduced. It is only important during the startup and stabilization period of the unit. The main use of heat (steam or fuel) is for the product fractionation section, and consumption will vary depending on the size and nature of the section.

The main electrical consumption is that of compressors (compressor for makeup hydrogen and recycle gas); it is lower in the case of processing light products than in the case of heavy products.

Table III.7 shows the average consumption rates reported in the literature for maximum gasoline production. It does not appear that these consumption rates are substantially modified in the case of middle distillate production.

Table III. 7: utility consumption in a hydrocracking unit

Utilities	350000 to 500000
Fuel, kcal/m^3	75 to 100
Electricity, kWh/m^3	25 to 50
Steam, kg/m^3	12 to 25
Cooling water, m^3/m^3	
Catalyst, kg/m^3	0.125 to 350
Estimate,F/m^3	2.2 to 6
Workforce	2 to 3 men/shift
Interview	4% of the investmentper year

III.5.1.2.2. Consumption of catalyst:

The consumption of catalyst for the Unicracking and Isocracking processes in catalytic reforming is estimated at 1kg for 3 to 8 m3 of charge. This relatively high consumption explains the high cost of the catalyst, which accounts for 20-30% of direct operating expenses. The catalyst cost for Unicracking is between 7 and 10 cts/bbl, while for Isocracking, it is around 15 to 20 cts/bbl, including chemicals. The catalyst's lifespan is around one year, and the spatial velocity is low. For Isocracking in two steps, the catalyst's cost is divided into approximately 25% for the first stage and 75% for the second stage.

III.5.1.2.3. Labor:

The labor force is estimated at 2 or 3 workers per position.

III.5.1.2.4. Maintenance:

The annual maintenance is estimated on average at 4% of the investment, which is a normal value for a refining process of this type.

The direct operating costs can therefore be estimated to be between 10F/m3. The lowest value corresponds to relatively mild treatments, such as the conversion of medium distillate to gasoline. The highest value corresponds to the conversion of vacuum distillates.

III.5.1.3.Hydrogen:

The availability of hydrogen is a significant problem in the catalytic reforming process. The theoretical availability of hydrogen from the reforming gas must be considered in relation to the necessary quantities. For the production of gasoline from medium distillate, the average hydrogen consumption is 280 m3/m3. However, the net production of hydrogen from a catalytic reforming unit is only around 80 m3/m3 of feedstock. This means that the amount of hydrogen available is only sufficient for a hydrocracking unit that is approximately four times smaller than the reforming unit. Other uses of hydrogen such as hydroprocessing and petrochemical production can further reduce the amount available. Therefore, it may be necessary to have an independent hydrogen production in many cases.

III.5.1.3.1. Total operating expenses:

In addition to the previously discussed expenses, indirect operating expenses (taxes, insurance, supervision, etc.) and capital charges (amortization and interest) must be added. If these expenses

are estimated at 16% of the investment, the total will be between 6F/m3 and 13.5F/m3. The estimated total operating expenses are summarized in Table III.8.

Table III. 8: total operating costs

Charge	Products	Total operating costs (F/m)
Heavy distillate (vacuum)	Medium distillate(max)	40 - 50
Heavy distillate	Fuel(max)	45 - 60
Medium distillate	Fuel(max)	35 - 50

Chapter IV: Simulation of Hydrocracking Unit using Aspen HYSYS

IV.1.Introduction

In this chapter, we utilize the Aspen HYSYS simulator to perform the simulation of the atmospheric residue hydrocracking process. The objective of employing this simulator is to obtain results that are closely aligned and feasible with the theoretical findings, thereby adding value to our work. By employing Aspen HYSYS, a widely recognized and extensively used process simulation software in the industry, we can accurately model and analyze the complex behavior of the hydrocracking unit. This simulation allows us to investigate various operating conditions, optimize the process parameters, and assess the performance of the hydrocracking unit. The integration of simulation results with the theoretical framework enhances our understanding of the hydrocracking process and facilitates the validation of our research findings. Through this chapter, we aim to present a comprehensive and reliable simulation study that contributes to the advancement and practical applicability of hydrocracking technologies.

IV.2.definition of hysys:

Aspen HYSYS is a powerful engineering simulation tool developed by Aspen Technology. It stands out due to its unique program architecture, interface design, engineering capabilities, and interactive operation. The integration of steady state and dynamic modeling capabilities within the same software is a significant advancement in the engineering software industry.

The software offers a comprehensive selection of operations and property methods, allowing users to confidently model a wide range of processes. This provides a powerful approach to steady state modeling, enabling engineers to simulate and optimize various process operations with confidence.

One of the key advantages of Aspen HYSYS is its ability to maximize the return on simulation time through increased process understanding. By using the software, engineers can gain insights into complex processes, identify optimization opportunities, and improve overall process performance.

Aspen HYSYS is widely used in industries such as oil and gas, chemical engineering, and refining. It provides a comprehensive platform for simulating and optimizing process operations, including distillation, reaction kinetics, heat exchangers, separators, and control systems. The software

incorporates rigorous thermodynamic models, advanced solver algorithms, and a user-friendly interface, making it an efficient tool for process simulation and optimization.

IV.3. Description of the Process in Aspen HYSYS :

To describe and execute the simulation of the atmospheric residue hydrocracking process using the Aspen HYSYS simulator, the following steps need to be followed:

V.3.1 introduction of the crude oil assay of Hassi Messaoud

The first step in simulating the hydrocracking process in Aspen HYSYS involves utilizing the crude oil assay of Hassi Messaoud to perform distillation and obtain the heavy distillate fraction.

In the simulation, the crude oil assay of Hassi Messaoud is used to define the composition and properties of the feedstock. This information is crucial for accurately modeling the behavior of the distillation unit within Aspen HYSYS.

	Whole Crude	Cut1	Cut2	Cut3	Cut4	Cut5	Cut6	Cut7	Cut8	Cut9	Cut10
Initial Temperature: (C)	IBP	IBP	40,0000	114,1176	188,2353	262,3529	336,4706	410,5882	484,7059	558,8235	632,9412
Final Temperature: (C)	FBP	40,0000	114,1176	188,2353	262,3529	336,4706	410,5882	484,7059	558,8235	632,9412	707,0588
StdLiquidDensity (kg/m...	801,2179	588,7940	703,3252	764,0390	803,7236	836,0791	861,7552	888,1544	910,2241	934,1526	963,5590
KinematicViscosity (cSt)...	2,994	0,300	0,726	1,195	2,517	5,996	23,095	129,487	762,545	4662,160	43589,888
KinematicViscosity (cSt)...	2,028	0,279	0,575	0,888	1,715	3,676	11,876	50,973	230,835	1107,955	7777,244
KinematicViscosity (cSt)...	1,705	0,268	0,518	0,778	1,445	2,963	8,899	34,127	137,831	593,365	3656,786
PourPoint (C)	11,811	-193,079	-169,807	-130,341	-55,790	-13,957	11,835	24,730	31,869	38,700	51,426
NaClByWt (%)	0,002	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,001	0,002
SulfurByWt (%)	0,042	0,000	0,000	0,000	0,000	0,012	0,073	0,118	0,133	0,143	0,156
MercaptanSulfurByWt (...	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,001	0,000	0,000	0,000
TotalAcidNumber (mg...	0,059	0,005	0,008	0,015	0,028	0,036	0,077	0,214	0,192	0,131	0,072

Figure IV. 1Petroleum assays sahara blend (bejaja) 2016

IV.3.2 Selection of the Thermodynamic Model "Fluid Package":

To study the properties of real gases or complex mixtures, there are equations of state that relate the equilibrium parameters of the system, especially in the domain of hydrocarbons. The equation supporting the ideal gas model is defined as follows:

$$P.V = n.R.T$$

However, this equation is not valid for real gases, which is why thermodynamic diagrams, tables of thermodynamic properties, or sets of equations of state covering the various pressure and temperature ranges are commonly used. Numerous equations of state have been proposed and continue to be developed. Among these equations, we can mention the Peng-Robinson equation, the Redlich-Kwong equation, and the Lee-Kesler-Plocker equation.

The equation of state generally used for hydrocarbons is the Peng-Robinson equation, which can be written as follows:

$$P = \frac{RT}{V - B} - \frac{a}{V^2 + 2Vb - b^2}$$

$$b = 0.0778 \frac{RTc}{Pc}$$

$$a = 0.45724 \frac{R^2Tc^2}{Pc}[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - Tr^{0.5})]^2$$

P: system pressure

Pc: critical pressure

Tc: critical temperature

T: temperature

V: molar volume of the gas

R: the universal gas constant: R = 8.3144621 J.K₋₁mol₋₁.

The Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations are widely used in the hydrocarbon industry, especially in refining and gas processing. Their advantages lie in the fact that they require minimal experimental data, have relatively short simulation times, and most importantly, they provide a good estimation of the liquid-vapor equilibrium for hydrocarbons. These equations are particularly important for process design.

In our study, we will utilize the Peng-Robinson equation as the chosen thermodynamic model or "fluid package" in Aspen HYSYS.
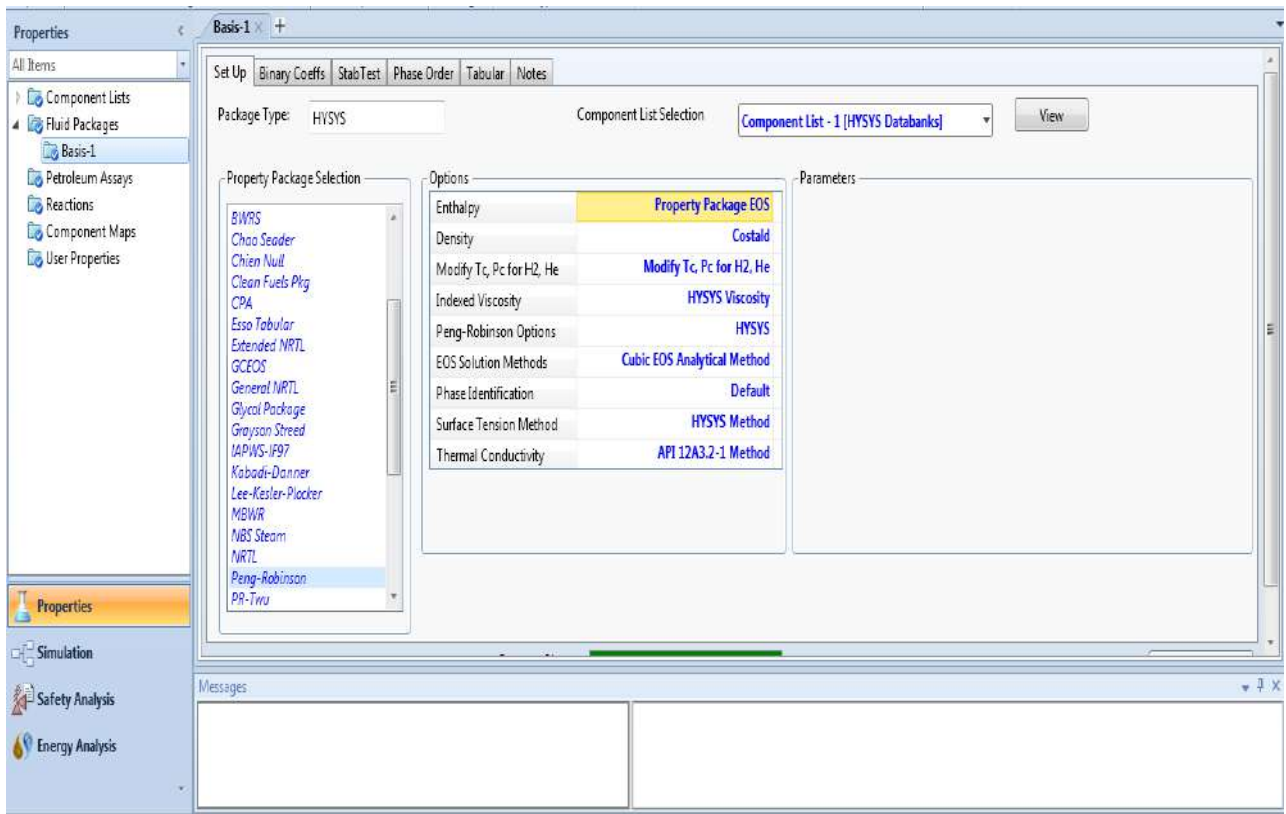
Figure IV. 2The choice of thermodynamic model (Peng-Robinson)

IV.3.3 Distillation of Crude Oil Feedstock for Heavy Distillate Fraction Recovery:

Using the distillation column model in Aspen HYSYS, the crude oil feedstock is subjected to the distillation process. The distillation column is configured with the appropriate parameters such as reflux ratio, tray efficiency, and temperature profiles to mimic the actual distillation unit at the refinery.

Through the distillation process, the feedstock is separated into various fractions based on their boiling points. The heavy distillate fraction, which is of particular interest for the hydrocracking process, is obtained as one of the outputs from the distillation column. This heavy distillate fraction contains the desired components that will undergo further conversion and upgrading in the hydrocracking unit.

V.3.4.Installation of the Hydrocracking Unit:

After obtaining the heavy distillate through the distillation step, the next phase involves the installation of the hydrocracking unit. This unit is designed to convert the heavy distillate into more valuable and lighter hydrocarbon products. we proceed to the simulation workspace, where we encounter the following window:

Figure IV. 3: Equipment Selection in the Simulation Workspace

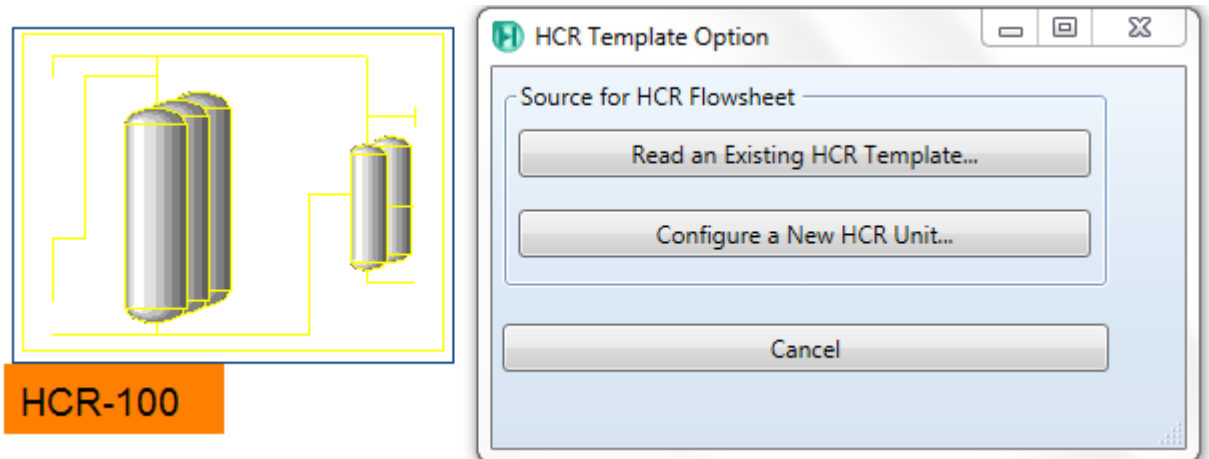"And we select the 'Hydrocracker' reactor and create a new hydrocracking unit."

Figure IV. 4: Creation of a New Hydrocracking Unit

IV.3.5.: Declaration of Hydrocracker Information in HYSYS:

IV.3.5.1: Declaration of Reactor and Catalyst Bed Count and Number of Stages:

In our unit, we have chosen a single stage with a reactor pair, and each reactor consists of two catalyst beds.
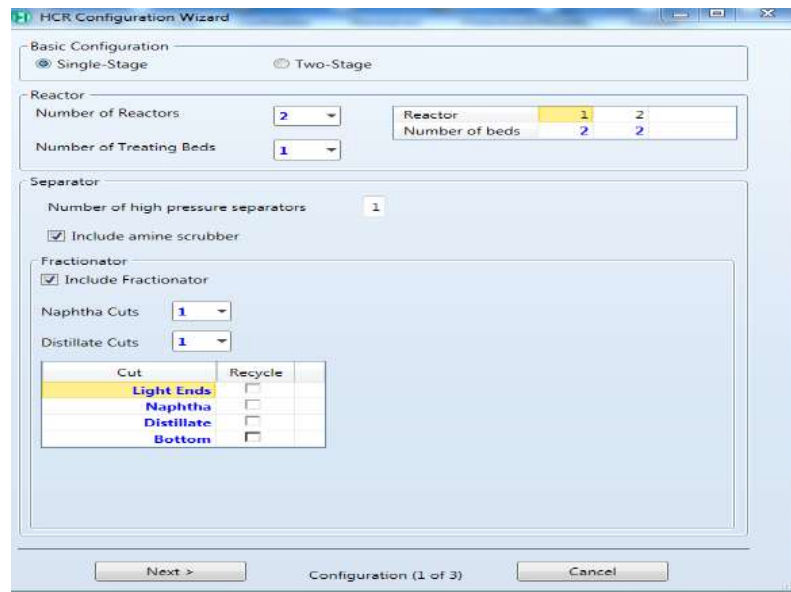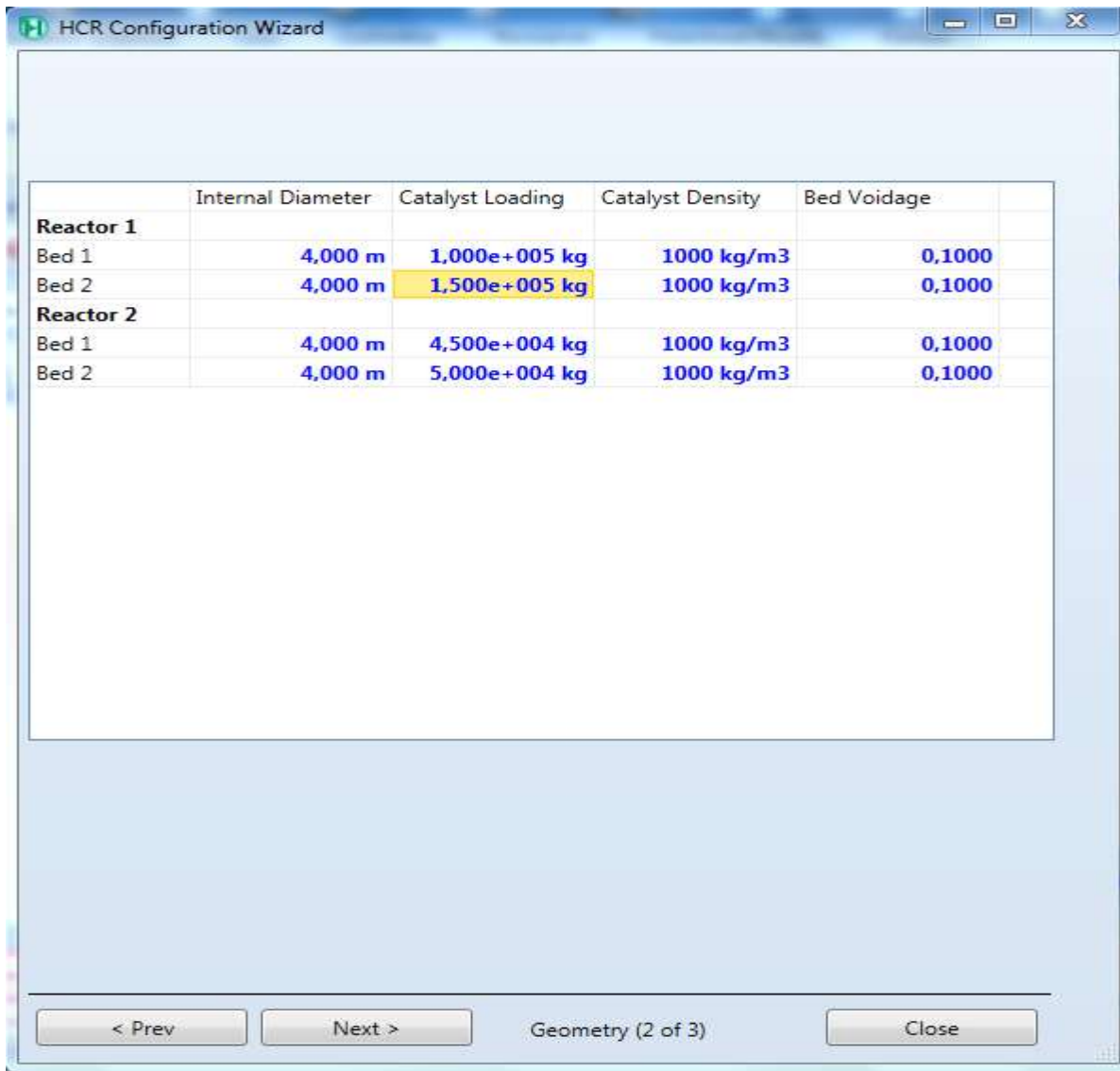

Figure IV. 5: Specification of Information for the Hydrocracking Unit

IV.3.5.2: Addition of Information on Reactors and Catalyst Used:

On the second page, we will add measurements regarding the catalytic reactors and the catalyst used. This includes the internal diameter for both reactors and for each of the two catalyst beds, as well as the charge volume, density, and catalyst voidage in each bed.

	Internal Diameter	Catalyst Loading	Catalyst Density	Bed Voidage
Reactor 1				
Bed 1	4,000 m	1,000e+005 kg	1000 kg/m3	0,1000
Bed 2	4,000 m	1,500e+005 kg	1000 kg/m3	0,1000
Reactor 2				
Bed 1	4,000 m	4,500e+004 kg	1000 kg/m3	0,1000
Bed 2	4,000 m	5,000e+004 kg	1000 kg/m3	0,1000

< Prev   Next >   Geometry (2 of 3)   Close

Figure IV. 6: Measurements of Reactors and Catalysts Used

IV.3.5.3: Addition of Measurements to Characterize the Feedstock Flow:

Now we need to declare the information about the feedstock for this unit (atmospheric residue). The information we will declare includes boiling points according to the D2887 distillation in different percentages (9 cases) to characterize the composition of the feedstock (atmospheric residue), API gravity which measures the fluid density relative to water, and the composition of nitrogen and sulfur present in the stream.

Figure IV. 7: Characterization of the Feedstock Flow - Part 1

Figure IV. 8: Characterization of the feed stream - Part 2

In this window (Operation - Feeds), we add additional information about the feedstock: volume, molar flow rate, temperature, and pressure in both reactors.

Figure IV. 9: Characterization of the Feedstock Flow - Part 3

In this window (Operation - Specifications), we add additional information and measurements about the feedstock and catalyst beds: the inlet and outlet temperatures in each bed, and the temperature difference between the pair of beds in each reactor.

IV.3.5.4. Addition of Characteristic Information about the Hydrogenation Gas:

In this window, we need to add measurements and information about the light component that needs to be injected (85% hydrogen gas), such as pressure, temperature, molar flow rate, and composition of the gas.
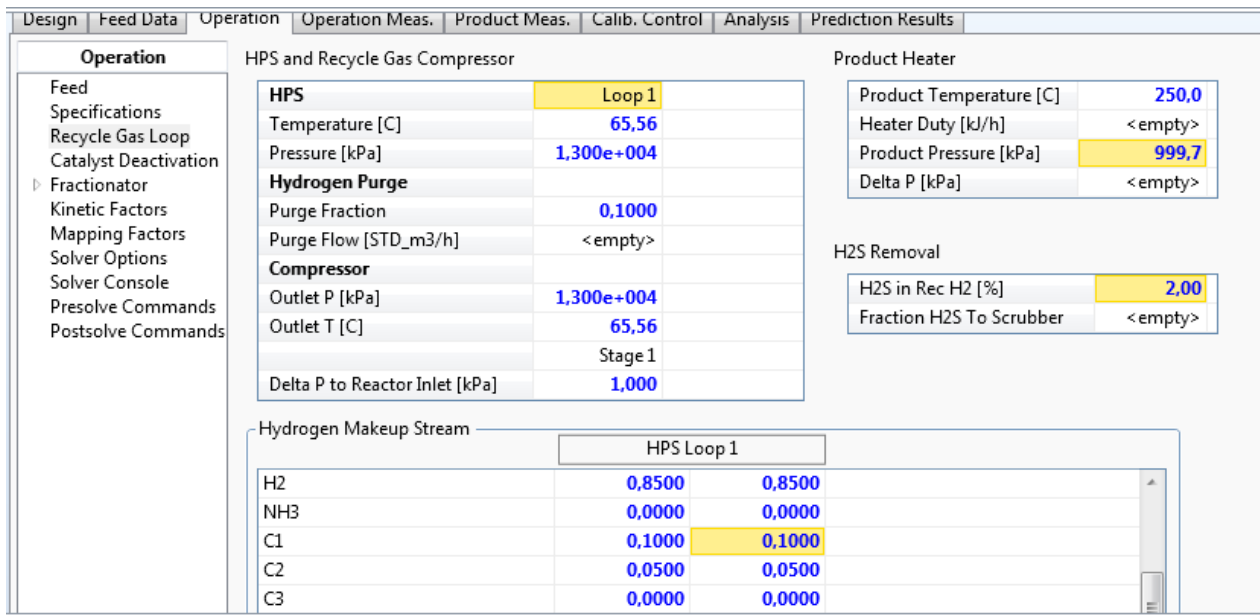
Figure IV. 10: Characterization of the Injection Gas Flow (Hydrogen)

IV.3.6: Addition of Measurements and Information about the Fractionation Column:

IV.3.6.1: Characterization of the Products from the Fractionation Column:

The products from the fractionation column are separated based on temperature. Each output product is characterized by its boiling temperature and different molar fractions.
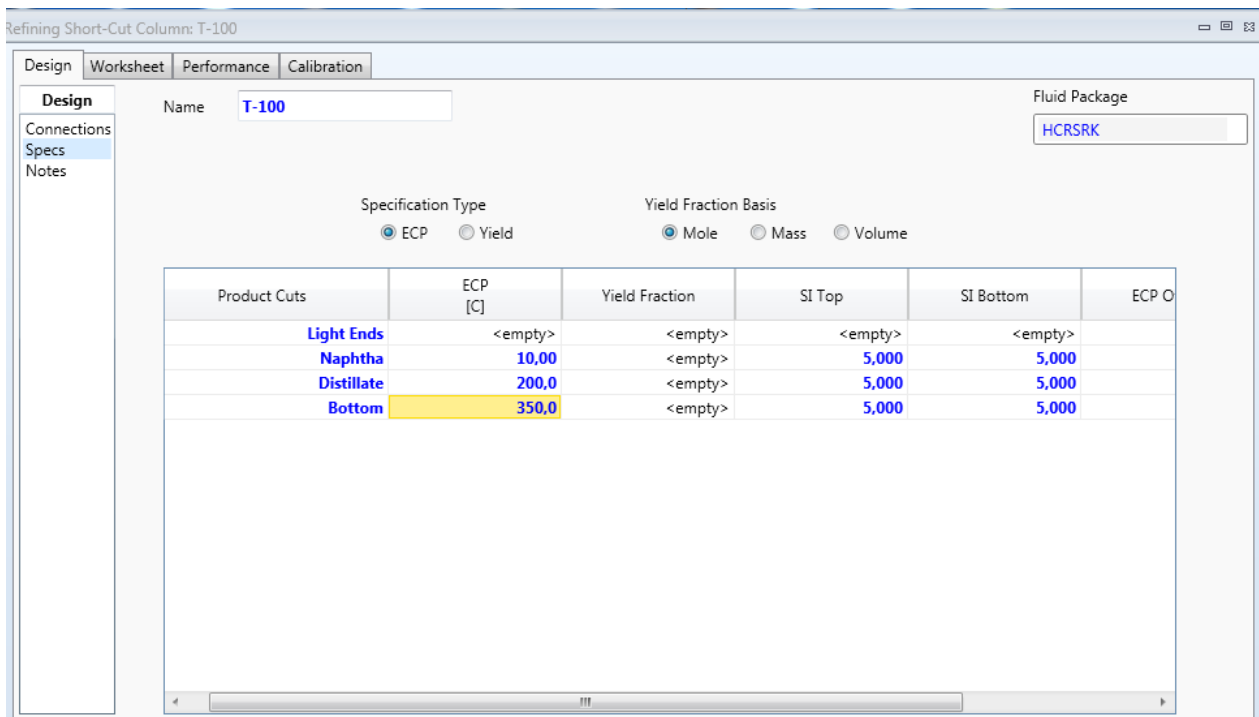
Figure IV. 11: Specification of the Outlet Products

IV.3.6.2: Addition of a Recycling Valve for Residue Rectification

We can also create a recycling loop within the residue to rectify the final products (the residue) in order to obtain superior purification results. This can be achieved by adding a recycling valve.
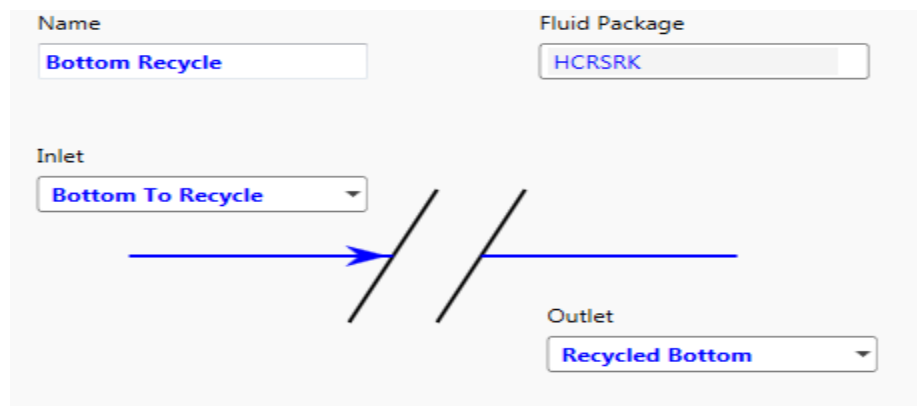
Figure IV. 12: Residue Recycling

IV.3.7: Final Process Flow Diagram (PFD):

The following figure illustrates the final process of the simulation for a complete hydrocracking unit.:
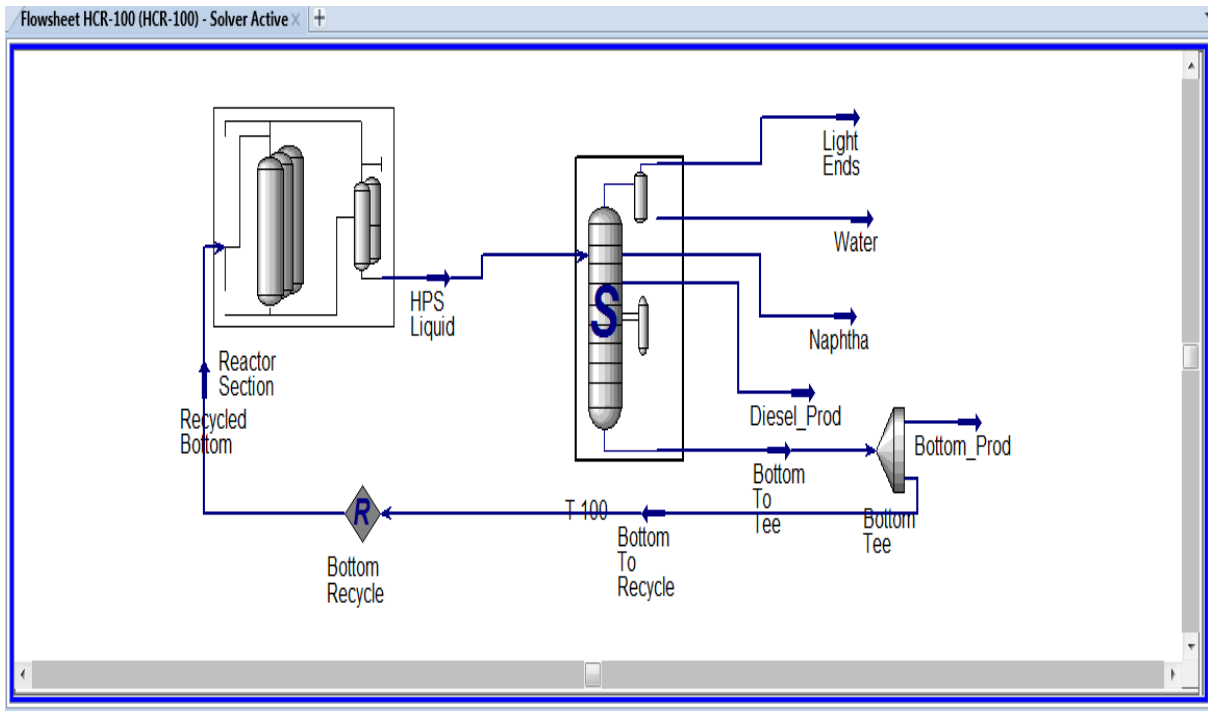
Figure IV. 13: Process Flow Diagram (PFD) final

IV.4: Interpretation of Obtained Results:

The following tables show the variation in composition and molar fractions of the outlet products.

IV.4.1: Light Ends:

It can be observed that the composition of the light ends varies between C1 and C5, with different fractions of vapor and liquid. Additionally, the presence of hydrogen gas (H2) and hydrogen sulfide (H2S) can be noted.

	ple Fractions	Vapour Phase	Liquid Phase
N2	0,0000	0,0000	0,0000
H2S	0,2312	0,2312	0,2265
H2	0,2823	0,2823	0,0021
NH3	0,0000	0,0000	0,0000
C1	0,2176	0,2176	0,0154
C2	0,1893	0,1893	0,1124
C3	0,0229	0,0229	0,0638
NC4	0,0248	0,0248	0,2779
C4	0,0275	0,0275	0,2207
NC5	0,0000	0,0000	0,0019
C5	0,0002	0,0002	0,0068
IC5-2	0,0042	0,0042	0,0721
C6P	0,0000	0,0000	0,0005
C6N	0,0000	0,0000	0,0000
C6A	0,0000	0,0000	0,0000
C7P	0,0000	0,0000	0,0000
C7N	0,0000	0,0000	0,0000
C7A	0,0000	0,0000	0,0000
LTH	0,0000	0,0000	0,0000
LBNIT	0,0000	0,0000	0,0000
C8P	0,0000	0,0000	0,0000
C8N	0,0000	0,0000	0,0000

Figure IV. 14: Composition of the Light Ends

IV.4.2: Naphtha

It can be observed that the composition of the Naphtha varies between C4 and C10, with different fractions of vapor and liquid.

	Mole Fractions	Liquid Phase	Vapour Phase
C2	0.0000	0.0000	0.0000
C3	0.0000	0.0000	0.0000
NC4	0.0091	0.0091	0.0350
C4	0.0011	0.0011	0.0047
NC5	0.0238	0.0238	0.0567
C5	0.0232	0.0232	0.0607
IC5-2	0.0113	0.0113	0.0372
C6P	0.2503	0.2503	0.4212
C6N	0.0107	0.0107	0.0150
C6A	0.0147	0.0147	0.0198
C7P	0.0449	0.0449	0.0479
C7N	0.0111	0.0111	0.0097
C7A	0.0159	0.0159	0.0132
LTH	0.0000	0.0000	0.0000
LBNIT	0.0000	0.0000	0.0000
C8P	0.2027	0.2027	0.1449
C8N	0.0234	0.0234	0.0148
C9P	0.0000	0.0000	0.0000
LNNIT	0.0000	0.0000	0.0000
C8A	0.0338	0.0338	0.0175
C9N	0.0234	0.0234	0.0081
LS8	0.0000	0.0000	0.0000
C9A	0.0380	0.0380	0.0119
C10P	0.0295	0.0295	0.0078
C10N	0.0238	0.0238	0.0049
C10A	0.0232	0.0232	0.0040
LTHA	0.0000	0.0000	0.0000
MBNITN	0.0000	0.0000	0.0000

Figure IV. 15: Composition of Naphtha

IV.4.3: Diesel

It can be observed that the composition of diesel (gasoil) varies between C10 and C16, with different fractions of vapor and liquid.

	Mole Fractions	Liquid Phase	Vapour Phase
HA1-OLEF	0,0000	0,0000	0,0000
HN1-OLEF	0,0000	0,0000	0,0000
C47-OLEF	0,0000	0,0000	0,0000
VA1-OLEF	0,0000	0,0000	0,0000
VN1-OLEF	0,0000	0,0000	0,0000
NC9	0,0000	0,0000	0,0000
IC9-1	0,0000	0,0000	0,0000
IC9-2	0,0000	0,0000	0,0000
NC11	0,0082	0,0082	0,0161
NC12	0,0225	0,0225	0,0379
NC16	0,0175	0,0175	0,0160
C10N-1	0,0077	0,0077	0,0135
C12N	0,0306	0,0306	0,0449
C14N	0,0264	0,0264	0,0282
C16N	0,0231	0,0231	0,0183
C12A	0,0173	0,0173	0,0246
C14A	0,0148	0,0148	0,0154
C16A	0,0129	0,0129	0,0100
IC10	0,0000	0,0000	0,0001
IC11	0,0020	0,0020	0,0040
IC12	0,0190	0,0190	0,0333
IC14	0,0200	0,0200	0,0263
IC16	0,0175	0,0175	0,0171
12N2	0,0255	0,0255	0,0354
14N2	0,0219	0,0219	0,0214
16N2	0,0191	0,0191	0,0143
H2O	0,0000	0,0000	0,0000

Figure IV. 16: Composition of Diesel

IV.4.4: Bottom (Residue)

It can be observed that the composition of the bottom (residue) varies, with different fractions of vapor and liquid.

	Mole Fractions	Liquid Phase	Vapour Phase
HN2	0,1169	0,1169	0,1242
HN3	0,0552	0,0552	0,0587
HN4	0,0327	0,0327	0,0343
MA2NHI	0,0013	0,0013	0,0013
HAN	0,2143	0,2143	0,2141
MANAHI	0,0005	0,0005	0,0005
HA2	0,0231	0,0231	0,0222
HAN2	0,0355	0,0355	0,0336
C26P	0,1928	0,1928	0,1799
HAN3	0,0217	0,0217	0,0201
HA2N	0,0199	0,0199	0,0175
HANA	0,0074	0,0074	0,0065
HA2N2	0,0060	0,0060	0,0052
HA3	0,0101	0,0101	0,0082
HTHAN	0,0013	0,0013	0,0010
HBNITAN	0,0023	0,0023	0,0018
HS28	0,0000	0,0000	0,0000
HTHA2	0,0056	0,0056	0,0042
HBNITA2	0,0000	0,0000	0,0000
HNNITA2	0,0000	0,0000	0,0000
HA4	0,0019	0,0019	0,0014
C47P	0,0001	0,0001	0,0001
VN1	0,0075	0,0075	0,0031
VA1	0,0012	0,0012	0,0005
VN2	0,0034	0,0034	0,0013
VN3	0,0020	0,0020	0,0007
VN4	0,0026	0,0026	0,0009
VAN	0,0009	0,0009	0,0003

| Total | 1,00000 | | |

Figure IV. 17: Composition of Residue

V.4.5 Water:

Note that the composition of the water is 100% H2O:

12N2	0,0000	0,0000	0,0000
14N2	0,0000	0,0000	0,0000
16N2	0,0000	0,0000	0,0000
H2O	1,0000	1,0000	1,0000

| Total | 1,00000 | | |

Figure IV. 18:Composition of Water

General Conclusion:

The main objective of our work on the valorization of heavy residue distillates through hydrocracking simulation using HYSYS was to study the role and benefits of hydrocracking in a refinery. Through the simulation, we successfully demonstrated the potential for valorizing heavy residue distillates and obtained highly acceptable results.

The simulation results confirmed that hydrogen plays a crucial role in facilitating chemical processes, and the hydrocracking process is highly effective in converting heavy residue into valuable and desirable products. The utilization of the atmospheric residue from the distillation column to obtain lighter and more usable products proved to be a promising approach for maximizing the value of the feedstock and reducing waste.

By using the HYSYS program, we were able to optimize the operating conditions and select appropriate catalysts, leading to improved product yields and quality. The simulation provided valuable insights into the behavior of real gases and complex mixtures, particularly hydrocarbons, thanks to the use of the Peng-Robinson equation as the thermodynamic model.

The detailed characterization of the feedstock, including the crude oil assay from Hassi Messaoud and the distillation process, allowed for a realistic representation of the input composition. The specification of reactor and catalyst information, as well as the characterization of hydrogen gas injection, contributed to an accurate simulation of the hydrocracking process.

The Process Flow Diagram (PFD) for the complete hydrocracking unit provided a comprehensive visualization of the overall process, including the distillation, reactor units, and fractionation columns. The analysis of the composition of light ends, naphtha, diesel, residue, and water yielded valuable insights into the product distribution and composition variations.

In conclusion, our work highlights the potential of hydrocracking for the valorization of heavy residue distillates. The simulation using HYSYS allowed for the evaluation of different process parameters, optimization of the operation, and obtaining realistic results. This study contributes to the understanding of the hydrocracking process and serves as a foundation for further research and development in the field of petroleum refining.

Reference:

1. Gary, J. H., & Handwerk, G. E. (2018). Petroleum Refining: Technology and Economics. CRC Press.

2. Gary, J. H., & Handwerk, G. E. (2007). Petroleum Refining: Technology and Economics (Fifth Edition). CRC Press

3. Gounder, R. M. (Ed.). (2019). Processing of heavy crude oils: Challenges and opportunities. IntechOpen.

4. Wauquier, J.P. (1998). Le Raffinage du Pétrole, Procédés de séparation.

5. Lei, Z., Chen, B., & Ding, Z. (2005). Special Distillation Processes.

6. Wuithier, P. (1972). Le pétrole: Raffinage et Génie Chimique. Technip.

7. Editions Technip. (1998). Le raffinage du pétrole: Procédés de transformation. 3

8. Kamaruddin, A. H. M. (2013). Aspen hysys: An introduction to chemical engineering simulation. LAP Lambert Academic Publishing.

9. Documents from Hassi Messaoud Refinery RHM2