بِسْمِ اَللَّهِ اَلْرَحْمَنِ اَلْرَحِيْم

Sudan University of Science & Technology

College of Petroleum & Mining Engineering

Petroleum Transportation & Refining Engineering Department

INTEGRATION OF HYDROGEN SYSTEM IN KHARTOUM REFINERY COMPANY (KRC)

مكاملة منظومة الهيدروجين في شركة مصفاة الخرطوم

Submitted in partial fulfillment of the requirement to take degree B.Sc. in petroleum Transportation & Refining Engineering.

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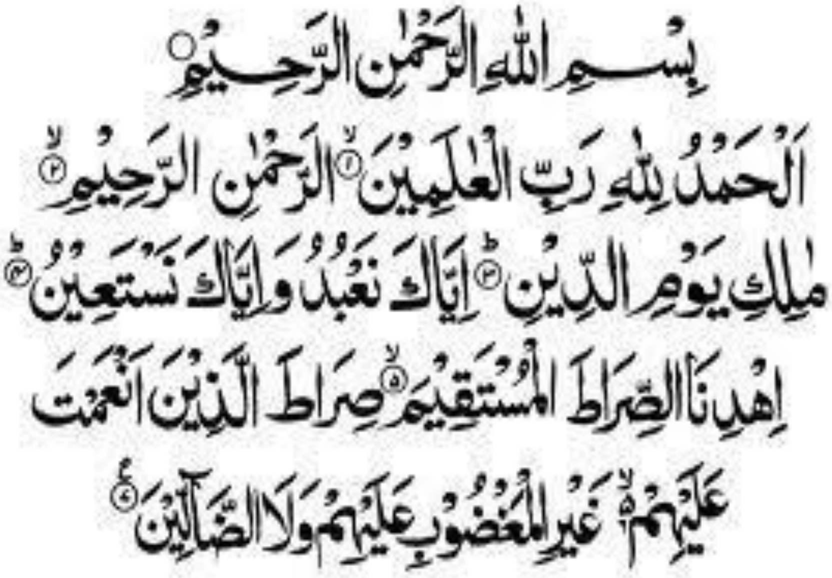
الإستهلال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Dedication

we would like to dedicate this research to our Dear parents.

To the people who paved our way of science and knowledge.

To the taste of the most beautiful moments with our friends.

Also we dedicate this research to our brothers and

sisters who spent their life to provide sufficient, Happiness and love.

Finally we dedicate this research to our colleagues In Transportation and refining department,

To all batch 25th petroleum engineering Students. And all batch7th refining engineering.

Acknowledgement

Eng.MohamPraise be to Allah until the praise reaches it is limit and thanks to him for his many blessings and to him is attributed all the credit for completing this work. Thanks and appreciation to Dr. Zainab Abdallah who will not be fulfilled by any word, for her guidance and support for us in completing this research, also thanks are due to all our teachers who taught us at their hand in all stages of our studies. And we are grateful to Eng.Abdallah shuaib and Ahmed Alriah .

Abstract

Environmental restrictions, new transportation fuels specification, and increased processing of heavier sour crude are leading substantial increases refinery hydrogen consumption for hydro desulphurization, aromatic and olefin saturation and improvement of product quality. All this factors make hydrogen management critical issue.

The objective of this study is managed the hydrogen in production and consumption units (**By using Aspen Hysys Simulation Software for CCR &DHT In KRC**).

The result showed improve quality of gasoline & diesel, and also showed excess in hydrogen which achieve more profit for refinery.

التجريد

تؤدي القيود البيئية والموصفات الجديدة لوقود النقل ، والمعالجة المتزايدة للخام الحمضي الثقيل إلى زيادة كبيرة في إستهلاك الهيدروجين في المصفاة لإزالة الكبريت بالهيدروجين والتشبع العطري والأوليفين وتحسين جودة المنتج ؛ كل هذه العوامل تجعل إدارة الهيدروجين قضية حرجة.

الهدف من هذه الدراسة هو إدارة الهيروجين في وحدات الإنتاج والإستهلاك بإستخدام برنامج المحاكاة Aspen Hysys في وحدتي (CCR & DHT).

أظهرت النتائج تحسين جودة البنزين والديزل ، كما أظهرت الزيادة من انتاج الهيدروجين ، مما يحقق ربحا أكبر للمصفاة.

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Chapter 1

Introduction

1.1. Hydrogen:

Matter exists in nature in three main forms: gases, liquids and solids, each of which has a set of properties that affect its use in our daily lives, and there are many gases that are highly concentrated in the layers of the atmosphere.

The most prominent gases in the atmosphere are hydrogen, and this gas is necessary and important for humans and animals. This gas is the lightest chemical element on Earth. This gas is considered the most abundant gas in the universe, as it occupies seventy-five percent of the volume of the universe. Most of the global hydrogen supply is obtained from fossil natural gas.

1.2. Hydrogen as Fuel:

Hydrogen gas is characterized by a number of important characteristics that qualify it to be the "fuel of the future." Directly or when mixed with natural gas in specified proportions .Non-Conventional Energy Sources, such as solar and hydrogen energy will remain available for infinite period. One of the reasons of great worry for all of us is reducing sources of conventional energies. The rate of fossil fuel consumption is higher than the rate of the fossil fuel production by the nature. The results will be the scarcity of automobile fuel in the world which will create lot of problems in transport sector. The other aspect is pollution added by these sources in our environment which increases with more use of these sources, resulting in the poor quality of life on this planet. There is constant search of alternate fuel to solve energy shortage which can provide us energy without pollution. Hence most frequently discussed source is hydrogen which when burnt in air produces a clean form of energy. In the last one decade hydrogen has attracted worldwide interest as a secondary energy carrier. This has generated comprehensive investigations on the technology involved and how to solve the problems of production, storage and transportation of hydrogen. The interest in hydrogen as energy of the future is due to it being a clean energy, most abundant element in the universe, the lightest fuel, richest in energy per unit mass and unlike electricity, it can be easily stored. Hydrogen gas is now considered to be the most promising fuel of the future. In future it will be used in various applications, e.g. it can generate Electricity, useful in cooking food, fuel for automobiles, hydrogen powered industries, Jet Planes, Hydrogen Village and for all our domestic energy requirements (**Hydrogen the fuel for 21st century).**

1.3. Physical Properties of Hydrogen:

Hydrogen is the smallest chemical element because it consists of only one proton in its nucleus. Its symbol is (H), and its atomic number is 1. It has an average atomic weight of 1.0079 , making it the lightest element. Hydrogen is the most abundant chemical substance in the universe, especially in stars and gas giant planets. However, mono atomic hydrogen is rare on Earth is rare due to its propensity to form covalent bonds with most elements. At standard temperature and pressure, hydrogen is a nontoxic, nonmetallic, odorless, tasteless, colorless, and highly combustible diatomic gas with the molecular formula H_2. Hydrogen is also prevalent on Earth in the form of chemical compounds such as hydrocarbons and water (1)

Hydrogen has one proton and one electron; the most common isotope, proton (^{1}H), has no neutrons. Hydrogen has a melting point of -259.14 °C and a boiling point of -252.87 °C. Hydrogen has a density of 0.08988 g/L, making it less dense than air. It has two distinct oxidation states, (+1, -1), which make it able to act as both an oxidizing and a reducing agent. Its covalent radius is 31.5pm.

Hydrogen exists in two different spin isomers of hydrogen diatomic molecules that differ by the relative spin of their nuclei. The otho hydrogen form has parallel spins; the parahydrogen form has antiparallel spins. At standard temperature and pressure, hydrogen gas consists of 75 percent orthohydrogen and 25 percent Para hydrogen. Hydrogen is available in different forms, such as compressed gaseous hydrogen, liquid hydrogen, and slush hydrogen (composed of liquid and solid), as well as solid and metallic forms.

1.4. Chemical Properties of Hydrogen:

Hydrogen gas (H_2) is highly flammable and will burn in air at a very wide range of concentrations between 4 percent and 75 percent by volume. The enthalpy of combustion for hydrogen is -286 kJ/mole, hydrogen gas can also explode in a mixture of chlorine (from 5 to 95 percent). These mixtures can explode in response to a spark, heat, or even sunlight. The hydrogen auto ignition temperature (the temperature at which spontaneous combustion will occur) is 500 °C. Pure hydrogen-oxygen flames emit ultraviolet light and are invisible to the naked eye. As such, the detection of a burning hydrogen leak is dangerous and requires a flame detector. Because hydrogen is buoyant in air, hydrogen flames ascend rapidly and cause less damage than hydrocarbon fires. H_2 reacts with oxidizing elements, which in turn react spontaneously and violently with chlorine and fluorine to form the corresponding hydrogen halides.

Hydrogen as a fuel has already found applications in experimental cars and all the major car companies are in competition to build a commercial car and most probably they may market hydrogen fuel automobiles in near future but at a higher cost compared to gasoline cars but it is expected that with time the cost of hydrogen run cars will decrease with time. Long lasting, light and clean metal hydride batteries are already commercial for lap top computers. Larger capacity batteries are being developed for electrical cars. Hydrogen is already being used as the fuel of choice for space programmers around the world. It will be used to power aerospace transports to build the international space station, as well as to provide electricity and portable water for its inhabitants. Present article deals with the storage and applications of hydrogen in the present energy scenario(2).

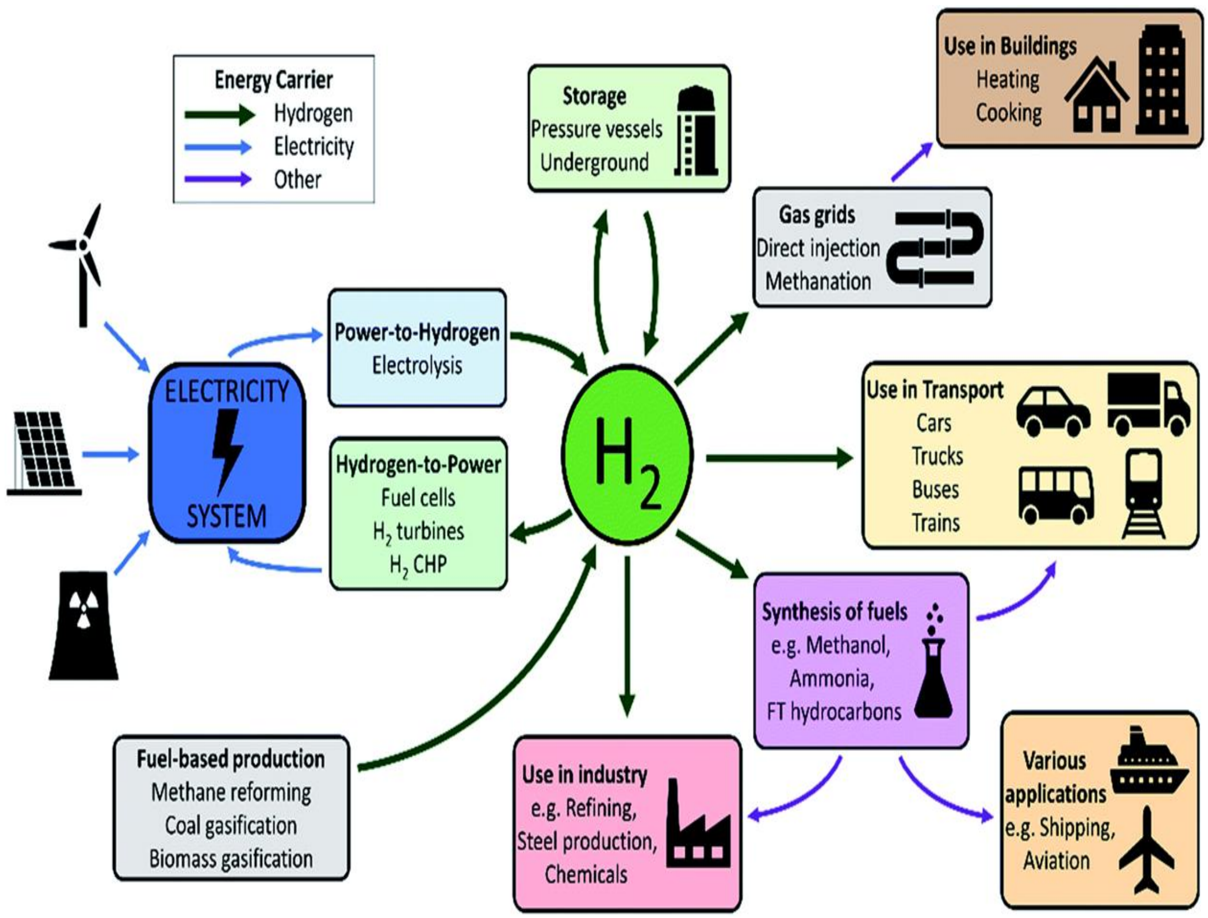


Figure: 1.1. The different uses of hydrogen.

1.5. Uses of Hydrogen:

1.5.1. Historical Industrial Applications:

For decades, hydrogen has been used primarily by the chemical and refining industries. End applications include:

For decades, hydrogen has been used primarily by the chemical and refining industries. End applications include:

Agricultural/Chemical Industry:

Hydrogen is a fundamental raw material needed to produce ammonia (NH3), also known as azane, an important part of fertilizers used in agricultural industries around the world. Ammonia can also be used as an affordable, environmentally-friendly refrigerant (R-717).

Petroleum Refining Industry:

Hydrogen is commonly used in hydrocracking to create petroleum products, including gasoline and diesel. It is also used to remove contaminants like sulphur and to create methanol (CH3OH).

1.5.2. Others Common Industry Applications of Hydrogen:

Hydrogen also has a long history of use in several other industries. These include:

1.5.2.1. Food:

Hydrogen is used to turn unsaturated fats into to saturated oils and fats, including hydrogenated vegetable oils like margarine and butter spreads.

1.5.2.2. Metalworking:

Hydrogen is used in multiple applications including metal alloying and iron flash making.

1.5.2.3 Welding:

Atomic hydrogen welding (AHW) is a type of arc welding which utilizes hydrogen environment.

1.5.2.4. Flat Glass Production:

A mixture of hydrogen and nitrogen is used to prevent oxidation and therefore defects during manufacturing.

1.5.2.5. Electronics Manufacturing:

As an efficient reducing and etching agent, hydrogen is used to create semiconductors, LEDs, displays, photovoltaic segments, and other electronics.

1.5.2.6. Medical:

Hydrogen is used to create hydrogen peroxide (H2O2). Recently, hydrogen gas has also been studied as a therapeutic gas for a number of different diseases.

1.5.3. Hydrogen Energy Industry Applications:

Newly commercialized applications of hydrogen, like fuel cells, are opening all kinds of new opportunities in transportation and other energy-related industries. In some applications, hydrogen is used as an alternative combustible fuel. Notable growth areas include:

1.5.3.1. Space Exploration:

Liquid hydrogen (LH2) fuel has played an important role in space exploration since NASA's Apollo program, when it was first used in in the secondary stage of the Saturn rockets. Today its use is expanding to include government and commercial organizations like United Launch Alliance, Boeing, and Blue Origin.

1.5.3.2. Aviation:

Several experimental programs have utilized hydrogen fuel cells in projects like the Pathfinder and Helios unmanned long duration aircraft. Recently, Airbus unveiled concepts for hydrogen-fueled "Zero" aircraft that utilize liquid hydrogen to power modified gas turbine engines.

1.5.3.3. Global Logistics:

Dozens of companies with large warehouse and distribution needs are turning to hydrogen fuel cells to power trucks, forklifts, and more. Companies like Nikola Motors, Hyundai, Toyota, Kenworth Truck Co, and UPS have big aspirations for hydrogen powered trucks, vans, and semis.

1.5.3.4. Public Transportation:

Hydrogen fuel cells are also being considered for other public transportation applications including trains and buses. Several major cities including Chicago, Vancouver, London, and Beijing have experimented with hydrogen powered buses. Hydrogen-powered trains have now appeared in Germany, and in the next five years, other models are expected to come to Great Britain, France, Italy, Japan, South Korea, and the United States.

1.5.3.5. Personal Transportation:

Nine of the major auto manufacturers are developing hydrogen fuel cell vehicles (FCVs) designed for personal use.

1.5.3.6. Power Generation:

Hydrogen is already used for cooling power plant generators, but it also provides a promising means of electrical grid stabilization. Electrical energy can be turned into hydrogen through electrolysis, then stored and used in an end-use application like transportation.

1.5.3.7. Backup Power Generation:

At a local level, stationary fuel cells are used as part of uninterruptible power supply (UPS) systems, where continuous uptime is critical. Both hospitals and data centers are increasingly looking to hydrogen to meet their uninterruptible power supply needs.(**Hydrogen Applications in industry –WHA International ,Inc** <https://wha-international.com/hydrogen-in-industry/>)(3).

1.6. Hydrogen Demand:

Refineries use hydrogen to lower the sulfur content of diesel fuel. Refinery demand for hydrogen has increased as demand for diesel fuel has risen both domestically and internationally, and as sulfur-content regulations have become more stringent. EIA data show that much of the growth in hydrogen use at refineries is being met through hydrogen purchased from merchant suppliers rather than from increased hydrogen production on-site at the refinery. The increased use of purchased hydrogen has implications for the refining industry's use of natural gas as a feed stock (4).

There are two forms of hydrogen production: on-purpose hydrogen production using steam methane reformers (SMR), and hydrogen production as a by-product of other chemical processes. Natural gas is used almost exclusively as feedstock for on-purpose hydrogen production in SMR units in the United States. Refineries, industrial gas producers, and other chemical manufacturers all use the same SMR technology, which is 90% efficient in produce hydrogen By-product hydrogen can be obtained from a chemical plant or other facility for which hydrogen is not the main product. In the chemical industry, for example, the chlor-alkali industry produces hydrogen as a by-product of chlorine production, and petrochemical plants release hydrogen as a by-product of their olefin production. Refineries also produce some by-product hydrogen from the catalytic reforming of naphtha into higher value high-octane products, but that supply meets only a fraction of their hydrogen needs.EIA surveys petroleum refineries and provides estimates of net hydrogen demand at the refinery, natural gas feed stock used to produce hydrogen, and hydrogen production capacity on an annual basis. Because the total amount of hydrogen demand is known, and on-site production in the refinery SMR can be derived from the surveyed natural gas feed stock requirements based on the known characteristics of the SMR process, the amount of merchant hydrogen supplied can be calculated by subtracting this on-site production of hydrogen from total refinery hydrogen demand.

Global demand for hydrogen has tripled since the 1970s see the chart below:

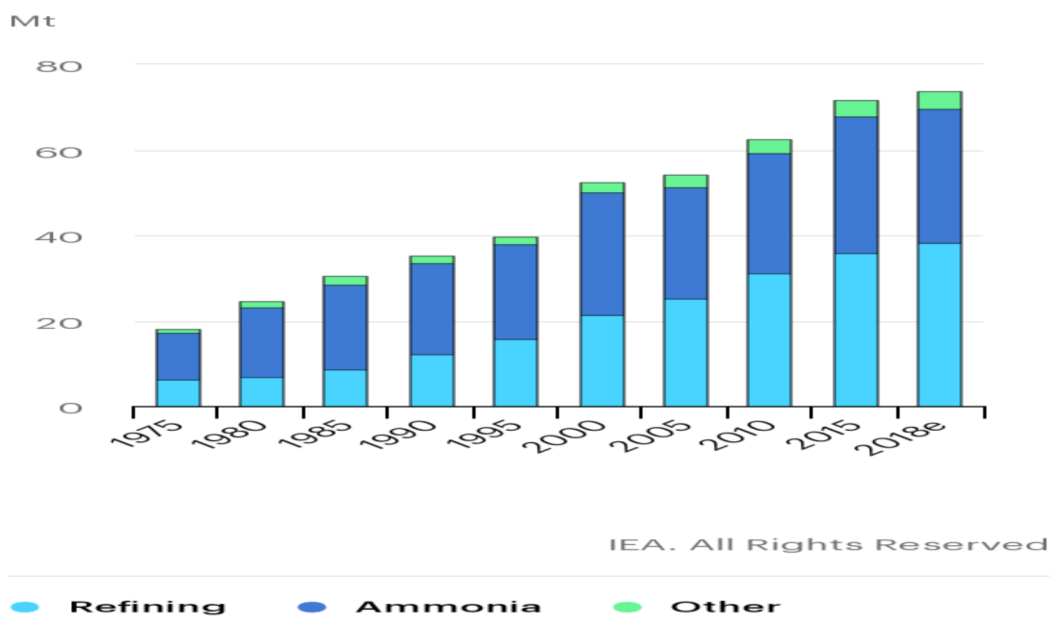


Figure: 1.2. Global Demand for Hydrogen (source: IEA).

1.7 Problem Statement:

Management of hydrogen in khartoum refinery company (KRC) , and increase The demand of hydrogen in refinery hydr treating unit which require provide excess of hydrogen production .

1.8 Objectives:

1. Management of hydrogen network.

2. Reducing the impurities to the minimum limit according to international standard specification by using hydrogenation technology.

3. Improve the quality of produced gasoline and diesel.

Chapter 2

2. Background and Literature review

2.1. Background:

An oil refinery or petroleum refinery is an industrial process plant purposely built for transformation and refining of crude oil into more useful products such as gasoline, diesel fuel, heating oil, kerosene, liquefied petroleum gas, jet fuel, asphalt base, heating oil, and fuel oils. Although each refinery has its unique features, it is a massive structure with different components, including the processing and distillation units. Also it consists of other structures such as storage facilities where refiners store crude oil and refined petroleum products.

A complex structure usually built on several acres of land an oil refinery runs 24 hours a day and 365 days a year. Running a refinery does not only require employing several people to monitor different plant units but also demands enough workforce to cope with its continuous operations, Crude oil in its raw state is of little or no value until we take it through the refining processes and transform it into various usable products.

2.1.1. Top Four Types of Oil Refinery:

There are four types of refineries – topping, hydro-skimming, conversion, and deep conversion refineries. Depending on the market a refiner is aiming at, each refinery has its unique design to ensure their production conforms to their host country’s set standards.

2.1.1.1. Topping Oil Refinery:

Topping refinery is a processing plant with a simple configuration. Constructed primarily for preparing raw materials for manufacturing petrochemicals and industrial fuels, a topping refinery serves better in areas where there are less refining regulations.

Topping refineries comprise facilities such as tanks, distillation units, gas, light hydrocarbons recovery facilities, and other necessary utility systems. However, they produce high volumes of poorly-refined oil because they lack the required processing units to reduce sulfur levels. Also, their outputs are usually limited to domestic markets.

2.1.1.2. Hydro-skimming Oil Refinery:

Hydro-skimming refineries refine better than topping refineries because of the addition of hydro treating and reforming units to the basic configuration that makes up a topping refinery. A refining plant with more capabilities, hydro skimming plants can produce refined products from little feed stock as well as high octane gasoline. Also, it can produce naphtha as well as hydrogen as by-products. The addition of a few other functional units such as hydro-treating, hydro-cracking, and a few others to hydro-skimming refineries make them more efficient than topping refineries. However, hydro-skimming plants may not deliver high-quality petroleum products as most of their outputs are usually residual fuels. Also, their low-quality output remains a challenge because more consumers are shying away from sulfur-filled petroleum products.

2.1.1.3.Conversion Oil Refineries:

Also known as cracking refineries, conversion refineries are refining plants that have all basic units that make up both topping and hydro-skimming refineries as well as gas oil conversion units. Also, additional units such as Olefin conversion plant and coking units are what makes them more efficient than hydro-skimming plants.

Furthermore, it has an additional beneficial feature which is reductions in the production of residual fuels. In other words, conversion oil refining plant produces lighter fuels such as gasoline, jet fuel, and diesel. It worth mentioning that light products are more profitable and environmentally friendly.

2.1.1.3.Deep conversion refineries:

A Deep Conversion refinery is a combination as all components of a conversion refinery, and an additional unit known as the coking unit. The cooking unit makes it possible to treat and convert extremely heavy crude oil fractions into lighter products.

Furthermore, it has an additional beneficial feature which is reductions in the production of residual fuels. In other words, conversion oil refining plant produces lighter fuels such as gasoline, jet fuel, and diesel. It worth mentioning that light products are more profitable and environmentally friendly

2.1.2. Types of crude oil:

Crude oil can be classified into three main types:-

A- Paraffin's.

B- naphthenes

C- aromatics

A. Paraffin's :

are series of hydrocarbons characterized by the rule that carbon atoms are connected by a single bond and other bonds are saturated with hydrogen

B. Naphthenes:

Naphthene or cycloparaffin hydrocarbon in which all of the available bonds of carbon atoms are saturated withhydrogen.

There are many types of naphthenes exist in crude oil but except for lower molecular weight compounds such as cyclopentane and cyclohexane etc.

C. Aromatics:

The aromatics hydrocarbon contain benzene ring which is unsaturated, the cyclo-hydrocarbons both naphthenic and aromatic, can add paraffin side chain in place of some hydrogen attached to the ring carbons and form mixed structure.

According to these types of crude oil a different requirement will be needed for hydro conversion processes.

2.1.3. Hydrogen Requirements in Modern Refineries:

Hydrogen is a key feed stock in many refining operations associated with the production of cleaner gasoline and diesel products. There are several drivers for the increase in hydrogen demand in the refining industry. Crude oil continues to become heavier with additional sulfur and nitrogen species. As the demand for heavy fuel oil diminishes, additional upgrading of the “bottoms” is required to produce a marketable fuel. More stringent environmental regulations have reduced the level of sulfur in both gasoline and diesel products. The combined effect of these trends is that refineries are running short of the necessary hydrogen to meet the increase in hydro treating and hydro cracking requirements.

2.1.4. Hydro conversion:

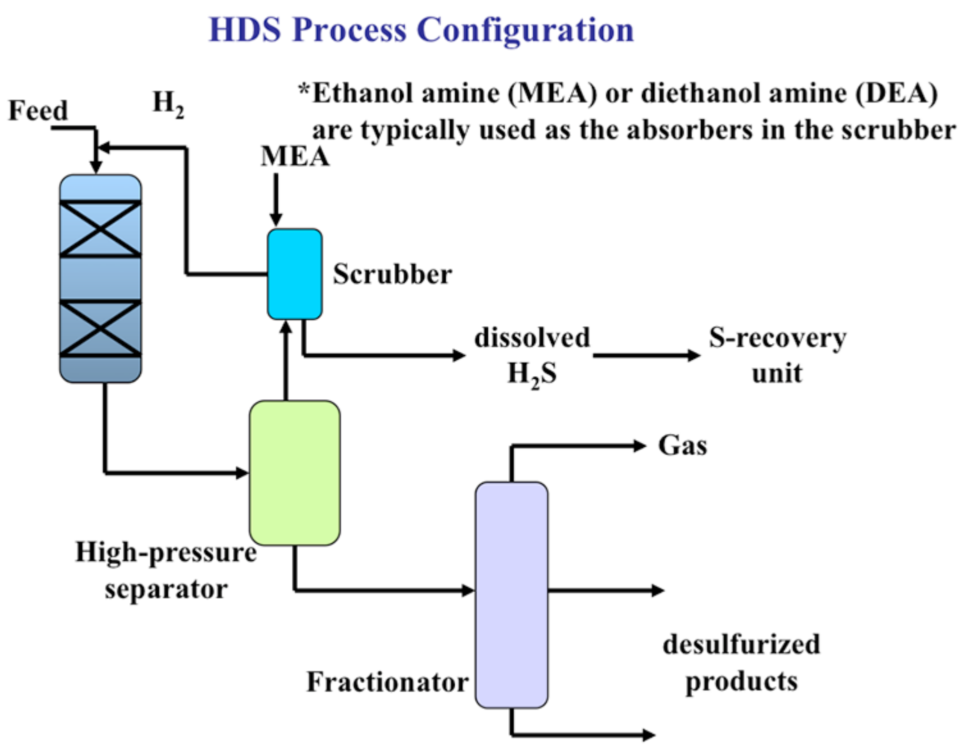
Hydro conversion is a term used to describe all different processes in which hydrocarbon reacts with hydrogen. It includes hydro treating, hydro cracking and hydrogenation. The term hydro treating is used to describe the process of the removal of Sulphur, nitrogen and metal impurities in the feed stock by hydrogen in the presence of a catalyst. Hydro cracking is the process of catalytic cracking of feed stock to products with lower boiling points by reacting them with hydrogen. Hydrogenation is used when aromatics are saturated by hydrogen to the corresponding naphthenes. The use of the hydro conversion technique depends on the type of feed stock and the desired products.

2.1.4.1-Hydrotreating:

Hydro treating achieves the following objectives:

A. Removing impurities, such as Sulphur, nitrogen and oxygen for the control of a final product specification or for the preparation of feed for further processing (naphtha reformer feed and FCC feed).

B. Removal of metals, usually in a separate guard catalytic reactor when the organo -metallic compounds are hydrogenated and decomposed, resulting in metal deposition on the catalyst pores (e.g. atmospheric residue desulphurization (ARDS) guard reactor). C.Saturation of olefins and their unstable compounds.



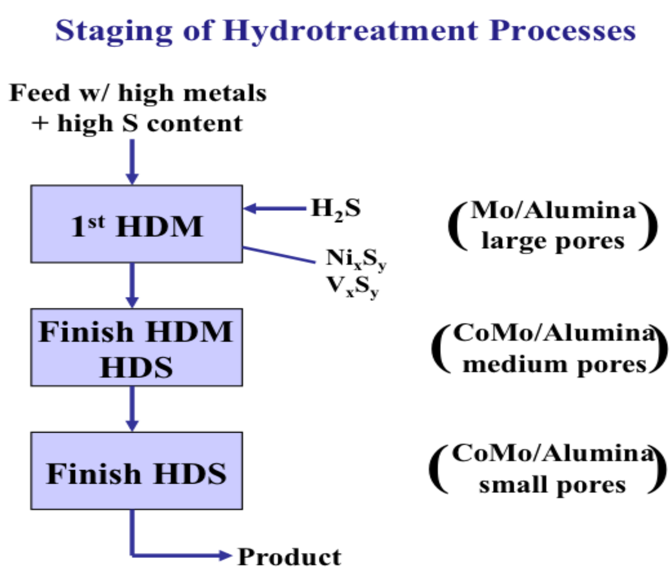


Figure: 2.1 Hydro treatment Process.(Source: Utton e- Education institute-Penn State 11/2021).

2.1.4.2. Hydro cracking:

Hydro cracking is a catalytic hydrogenation process in which high molecular weight feed stock's are converted and hydrogenated to lower molecular weight products. The catalyst used in hydro cracking is a bifunctional one. It is composed of a metallic part, which

Promotes hydrogenation, and an acid part, which promotes cracking. Hydrogenation removes impurities in the feed such as Sulphur, nitrogen and metals. Cracking will break bonds, and the resulting unsaturated products are consequently hydrogenated into stable compounds.

2.1.5. Hydrogen Production:

The production of hydrogen from hydrocarbons can be broken down into three key chemical reactions:

A. Steam-methane reforming.
B. Pressure Swing Adsorption (PSA).
C. Continuous catalytic regeneration reforming (CCR).

2.1.5.1. Steam-methane reforming (SMR):

Steam-methane reforming is commonly used on natural gas or naphtha feed stock, with later being an important source of hydrogen in refinery. We have assumed a natural gas feed stock. Natural gas is not a commodity with uniform composition, and the precise composition can have important implications for optimal plant design, to the high purity hydrogen product are: pretreatment of the raw feed, reforming to synthesis gas, conversion to a hydrogen-rich gas, and purification to hydrogen product specifications. This basic SMR process is supported by a process furnace, which provides heat to raise the gas temperature for the endothermic pre treatment and reforming processes. The furnace also provides heat to raise steam, which is used as a reagent in both reforming and gas conversion. Note that gas conversion, which is exothermic, also provides heat for raising steam. The furnace consumes natural gas as fuel and process gas, which is a residual from the hydrogen purification processes. The furnace also provides heat to raise steam, which is used as a reagent in both reforming and gas conversion. (20^{th} Annual International Pittsburgh Coal Conference September 15-19, 2003 Pittsburgh, PA).(6)

2.1.5.2. Pressure Swing Adsorption (PSA):

The use of the Pressure Swing Adsorption (PSA) process has seen tremendous growth during the last decades mainly due to its simplicity and low operating costs. (Hydrogen Recovery by PSA), Pressure swing adsorption (PSA) technology is an effective method to extract hydrogen from synthesis gas (syngas) and purify the produced hydrogen. The dynamic adsorption models for syngas (H_2 /CO 70/30 mol %) treatment by single- and double-bed PSA systems with zeolite 5A were developed, Double –bed process has better hydrogen purification performance than single – bed one. (zhang 2019), it is very important to remove other impurities (mainly CO, CO_2 and CH_4) using adsorption separation technology which is generally considered to be low in energy consumption and very precise in H_2 separation (99.99%) with the aid of pore size and surface characteristics of adsorbent. (yang 2008)(7).

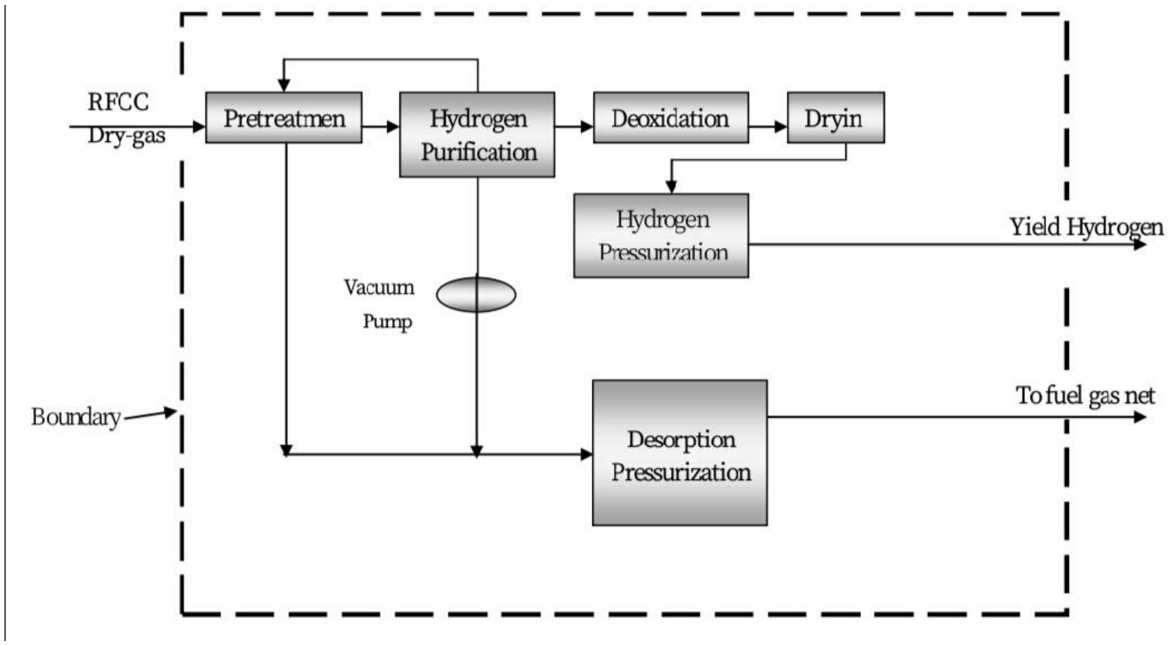


Figure: 2.2 Pressure Swing Adsorption (PSA). <Manual 2018>.

2.1.5.3 Continuous Catalytic Regeneration (CCR) Reforming:

Continuous Catalytic Regeneration (CCR) is one of the key processes in petroleum refineries for octane improvement and production of aromatic feed stock for petrochemical industries.

The Continuous Catalytic Regeneration (CCR) process consists of three or four adiabatic reactors in series with intermediate heaters (E. Bonabeau et al.,, 1999).Low octane hydrocarbons such as paraffin's and naphthenes are converted to high octane aromatics, Hydrogen and other light gases through this process (Ancheyta-Juarez J et al.,, 2000).According to modes of catalyst regeneration, Reforming processes are generally classified into three types: semi regenerative, cyclic and continuous regenerative process (D'Ippolito SA et al.,, 2008).(10)

Nowadays due to high catalyst activity, higher aromatic content, and high hydrogen purity, applying of Continuous Catalytic Regeneration (CCR) units have increased quickly respect to other type of reforming process (Donald, M. L et al, 1985)(11)

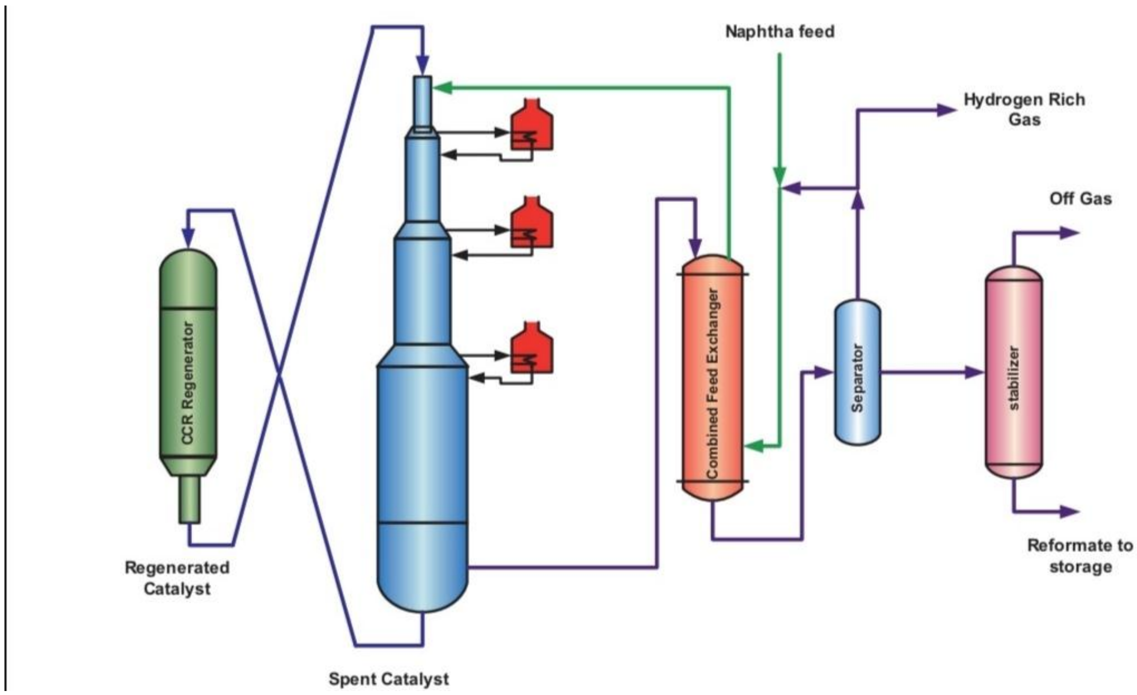


Figure: 2.3. Scheme process diagram of continuous catalyst regeneration reformer (CCR).(M.R. Rahimpour et al./Applied energy 109 (2013) 79-93)

Literature Review

2.2.1. Previous Studies:

In the refinery business, hydrogen is viewed as a utility that must be available to operate, like other utilities such as electricity and water. However, in this research, the development and implementation of a good overall management policy for the required hydrogen in the refinery will allow the handling of hydrogen as an asset for the refinery. Most of the publications about refinery hydrogen have focused on individual hydrogen production and/or consuming units rather on the overall hydrogen system.

Tremendous amount of work has been performed in the past in the area of hydrogen purification systems. There are many methods of purification systems in oil refineries, such as PSA, membrane separation, cryogenic separation, and liquid absorption. For example, Why sall and Picioccio (1999) explained the common purification methods in a refinery and presented criteria for selection and revamping each of them. Peramanu et al. (1999) continued by determining the options that were economically and technically suitable for PSA, membranes, and counter current gas-liquid contacting. All of this research is important, and in fact it has improved the refinery hydrogen system by modifying individual refinery processes and units. However, the whole refinery hydrogen system should be integrated in order to achieve more improvements.

A. The first study of the refinery hydrogen system was done by Towler et al. (1996). Towler et al. analyzed the hydrogen network from an economic point of view, and he compared the cost of recovering hydrogen and the value added by hydrogen in refinery processes. The pinch technique was applied, and the driving force to recover hydrogen was purely based on economics. However, the physical constraints that manipulate the network were not taken into account. The study nevertheless gave a great indication forresearchers to consider the whole network of the refinery hydrogen system.

B. Alves and Towler (2002) gave an excellent analysis of the hydrogen distribution system in a refinery. They identified the sources and sinks of hydrogen and proposed a systematic method for setting the target for the minimum supply of fresh hydrogen. Unfortunately, their study did not take into account the pressure constraint, which is a significant concern in the refinery hydrogen network.

C. Hallale and Liu (2001) introduced an efficient mathematical method for refineries to optimise a refinery hydrogen network to maximize the amount of hydrogen recovered throughout the refinery.

D. Zhang et al. (2001) studied a simultaneous optimisation for overall integration of the hydrogen network, the utility system, and the material processing system in a refinery. Zhang et al. used a linear programming (LP) model to represent the network, which prevented them from exploring the discrete components of the hydrogen network. Liu and Zhang (2004) proposed a systematic methodology for selecting appropriate purifier technology for the hydrogen network in the refinery and considered operating and capital costs in order to evaluate economic trade-offs.

From the previous discussion, it is apparent that there is a need for an efficient, integrated, refinery-planning model for petroleum products and the hydrogen network. It is imperative that the model should be able to provide production objectives and incorporates a proper hydrogen management strategy. The model should also represent refinery operation planning in such a way as to optimise the operating variables in individual processing units as well as to optimise hydrogen requirements. (**Int. J. Process Systems Engineering. Vol. 1, Nos. 3/4, 2011)(5).**

Chapter 3

3. Methodology & Material Balance:

3.1. Materials:

The data used in this research obtained from Khartoum refinery company (KRC) and it is properly used to perform the material and energy balance to the unit .

3.2. Methods:

3.2.1. Pressure swing Adsorption (PSA):

Adsorption theory and types: if two different phase state material meets, the molecule of low-density material will be adhered on the surface of high-density material. This phenomenon and process is called adsorption.

Adsorption can be divided into four main types. They are chemisorption, active sorption, capillary condensation, and physisorption.

Chemisorptions: there is chem.-reaction between adsorbent and adsorbate, which produces compound on the surface of adsorbent. This adsorption process called Chemisorption. Generally, this type of adsorption is very slow, and desorption process is very difficult also.

Active adsorption: it is the adsorption process of resulting surface complex compound between adsorbent and adsorbate , which also has quite difficult desorption process.

Capillary condensation: while solid adsorbent adsorbs vapor, there is coagulate phenomenon happens in the pore of adsorbent, it needs heating to complete regeneration.

Physisorption: this adsorption process relies on Van der Waals interaction between molecules of adsorbent and adsorbate. Its feature: there is no chem.- reaction during the adsorption process; the adsorption process is very fast; equilibrium of different phases- which involved adsorption process -can be completed within second;
also this adsorption is fully reversible. The main adsorption type of PSA Hydrogen Purification Equipment is Physisorption.

Table 3.1 RFCC Dry-gas:

Component	**mol%(v)**
H2	33.65
N2	13.90
O2	1.05
CH4	24.49
C2H4	14.58
C2H6	11.18
C3H6	0.70
C3H8	0.20
C4	0.20
H2o	0.05

Total	100
Temperature(C)	40
Pressure(*Map*)	0.7

Table 3.2.Product hydrogen specification:

Component	**H2**	**N2**	**CH4**	**H2O**	**O2**	**(CO+co 2)**	**Tota l**	**pressur e**	**Temperat ure**
Mol%(V)	99.10	0.61	0.10	0.19	<1oo ppm	<20 ppm	100	8.7 Mpa(G)	40 (C)

Table 3.3. The specification of desorption gas:

Component	**Mol%**
H2	18.46
N2	16.81
O2	1.08
CH4	29.84
C2H4	17.78
C2H6	63.36
C3H6	0.85
C3H8	0.24

C4	0.24
H2O	1.07
Total	100
Temperature(c)	40
Pressure(Map)	0.6

Material Balance:

This balance table only shows the design value. In practice, the actual quantities of material vary with the condition of feed gas.

Table: 3.4 PSA material balance.

Stream Number	1		2		3		4		5	
Stream Name	Dry-gas		Pre-treatment gas		Crude hydrogen		Product hydrogen		Desorption gas	
Component	Nm^3/h	Mol%	Nm^3/h	MOL%	Nm^3/h	Mol%	Nm^3/h	Mol%	Nm^3/h	Mol%
H2	3701.5	33.65	3701.5	33.73	2261.5	98.42	2220.9	99.29	1440	16.55
N2	1529	13.9	1529	13.93	13.6	0.59	13.6	0.61	1515.4	17.41
O2	115.5	1.05	115.5	1.06	20.3	0.9	≤10ppm	≤10ppm	95.2	1.09
CH4	2693.9	24.49	2693.9	24.55	2.3	0.1	2.3	0.1	2691.7	30.93
C2H4	1603.8	14.58	1603.8	14.61	-	-	-	-	1603.8	18.43
C2H6	1229.8	11.18	1229.8	11.21	-	-	-	-	1229.8	14.13
C3H6	77	0.7	70.5	0.65	-	-	-	-	77	0.88
C3H8	22	0.2	22	0.2	-	-	-	-	22	0.25
C4	22	0.2	5.5	0.05	-	-	-	-	22	0.25

H_2O	5.5	0.05	1.1	0.01	-	-	-	-	5.5	0.06
TOTAL	11000	100	10972	100	2297.7	100	2236.8	100	8702.3	100
Molecular weight (kg/mole)	16.79		16.71		2.36		2.22		20.6	
Mass flow rate(kg/h)	8245.1		8145.4		242.1		221.7		8003	

3.2.2. Diese**l Hydrotreating Unit (DHT):**

Process Description:

The catalytic diesel oil from tank farm is pumped under level control of feed stock surge drum via the feed stock relay pump, then, removes the particles bigger than 25μm through feed stock filter, and then, enters feedstock surge drum. The feed stock coming from surge drum boosts its pressure to 9.2MPa through hydro-treating feeding pump, then, exchanges heat through the reaction effluent/feed stock heat exchangers under flow rate control, then, blends with the mixed hydrogen and enters the reaction effluent/reaction feeding heat exchangers, and then, is heated to the reaction temperature through the reaction feeding heating furnace, and then, enters the hydro treating reactor. The reactor is set with two catalyst beds, between which is set with quench hydrogen.

The reaction effluent from reactor passes through heat exchanger and then, passes through reaction effluent air cooler and reaction effluent water cooler to cool down to 45℃, and then, enters the high pressure separator (HPS).

To prevent the ammonium salt in the reaction effluent from being separated out at low-temperature positions, desalted water will be injected into the pipeline at the upstream (or downstream) of last heat exchanger through water injection pump .

The cooled reaction effluent is collected in the cold HP separator where three phases are separated gas, hydrocarbon liquid and sour water. The gas phase (recycle hydrogen) goes to separates liquid through the knock out drum at the suction of the recycle hydrogen compressor, then, enters the recycle hydrogen side. In the make upside /circulating hydrogen compressor pressurize to 8.7MPa, then, is divided into two routes: one route is used as the reactor's quench hydrogen; the other route mixes with the make upside from the outlet of the make upside side, and the product hydrogen from the hydrogen recovery part. The mixed hydrogen will mix with the feed stock as the reaction feeding. The sour water containing ammonium salts is sent,to the sour water stripping unit.

The hydrocarbon liquid is sent to the low pressure separator (LPS) through the pressure reduction adjusting valve under liquid level control; then, the gas of flash distillation from LPS will be discharged to the fuel gas pipe network or flare.

The LPS-effluent oil passes through diesel oil/LPS-effluent oil heat exchangers exchanges heat with refined diesel oil and reaction effluent separately, then, enters diesel oil steam stripping tower. The low-pressure and high- pressure separators sourer water will be discharged from the unit together, but reflux drum sour water sent to sour water plant separately.

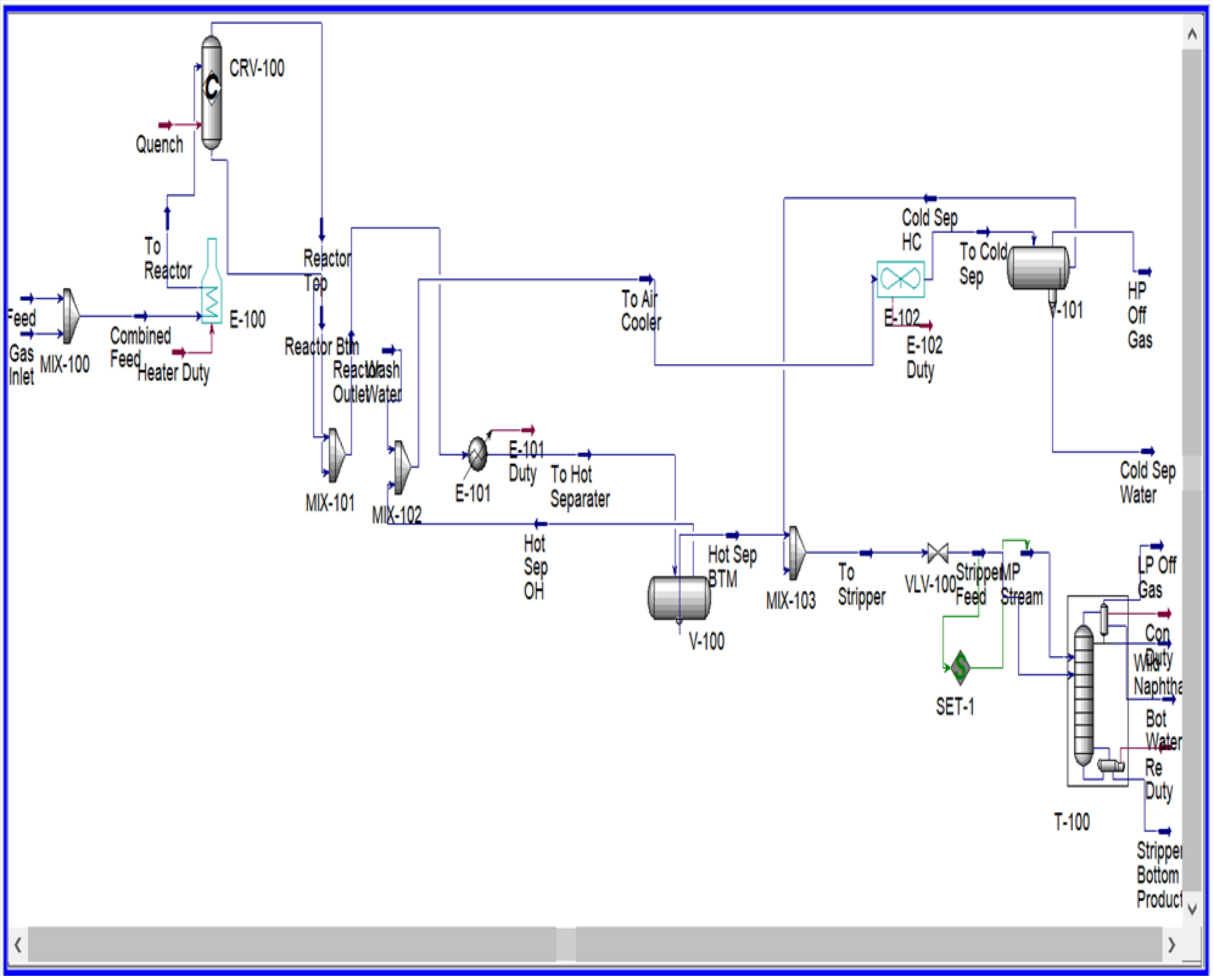


Figure:3.1. Diesel Hydrotreating Unit (DHT).

Diesel Feed Stock:

Table 3.5: RFCC Diesel Specification

Distillation range	204
10%	228
20%	242
30%	254

50%	278
70%	309
80%	323
90%	337
Sulfur, ppm	600
D, kg/m3	856
Nitrogen, ppm	283
Freezing point	-2
Bromine value mgBr/100g	15.4
Cetane index	33.0

Hydrogen:

The hydrogen source required by the unit is mainly provided by the reformed hydrogen from the reforming unit, and the insufficient part will be provided by the hydrogen from the hydrogen recovery part.

Table:3.6 Composition of Reformed Hydrogen:

Component	**H2**	**C1**	**C2**	**C3**	**iC4**	**nC4**	**C5+**	**Sum total**
V%	85.43	5.83	4.48	2.54	0.72	0.24	0.76	100

Table: 3.7 Composition of PSA Hydrogen:

Composition	H2	C1	N2	O2	H2O	Sum total
V%	>99.9	100ppm	20ppm	10ppm	50ppm	100

Table: 3.8 Material Balance of Diesel Hydrotreating Unit:

No.	Material Name	Measuring unit					
		Rate %		Kg/h		t/d	
		Nominal	Actual	Nominal	Actual	Nominal	Actual
	Input Part						
1	**Catalytic Diesel**	100	100	62500	54975	1500	1319.40
2	**Reformed Hydrogen**	2.36	2.39	1474	1317	35.38	31.61
3	**Hydrogen***	0.25	0.24	156	131	3.74	3.14
4	**Desalted water**	4.8	5.46	3000	3000	72.00	72.00
5	**Steam Stripping**	2.08	2.09	1300	1150	31.20	27.60
	Sum total	109.49	110.18	68430	60573	1642.3	1453.75
	Output Part						
1	**Refined Diesel Oil**	99.08	99.08	61925	54472	1486.2	1307.33
2	**Crude Gasoline**	1.03	1.03	644	568	15.46	13.63
3	**Low-Component**	0.66	0.64	411	351	9.86	8.42

4	**Tower Top Gas**	1.7	1.67	1060	920	25.44	22.08
5	**Acid Sewage**	6.55	7.29	4094	4008	98.26	96.19
6	**Oil-bearing**	0.30	0.30	188	167	4.51	4.01
7	**Loss**	0.17	0.17	108	87	2.59	2.09
	Sum total	109.49	110.18	68430	60573	1642.3	1453.75

3.2.3. Continuous Catalytic Reforming (CCR):

Process Description:

The purpose of the CCR unit is to produce a high octane number reformate, which is a main component of the gasoline pool, and a hydrogen rich gas CCR unit feed is hydrotreated Coker Naphtha that has low potential aromatics content (26.98 wt%) mixed with straight run Naphtha.

Due to the presence of contaminants in all cases, more or less elaborated naphtha pre treating is always necessary.

CCR unit is a catalytic reforming process of naphtha, based on AXENS's licensed technology. It includes two sections:

• The naphtha catalytic reforming itself, including, reactors heaters, effluent recovery and stabilization.

• The catalyst circulation and regeneration which involve solid handling and moving bed technology.

The reforming reactions take place in moving bed catalytic reactors from which the catalyst is withdrawn, then regenerated and recycled. The catalyst circulation and regeneration are performed on a continuous basis with full automatic control of all the operations.

A high temperature (in the range of 500°C) is required to promote the chemical reactions which improve octane number; Hence the need for a preheating of the feed.

Moreover, some of the desirable reactions are highly endothermic. This leads to split the bulk of the catalyst into several reactors with intermediate heaters.

The high performance of the CCR unit process is largely owed to low pressure operation coupled with high temperatures; which, in conventional fixed bed reactors would lead to very short cycle length. Hence CCR unit involves continuous catalyst regeneration.

Configuration Of The Unit:

This unit consists of several components, including

- Pre treatment section .
- Reforming section.
- Catalyst regeneration section.
- Utilities section .
- Waste heat boiler section.

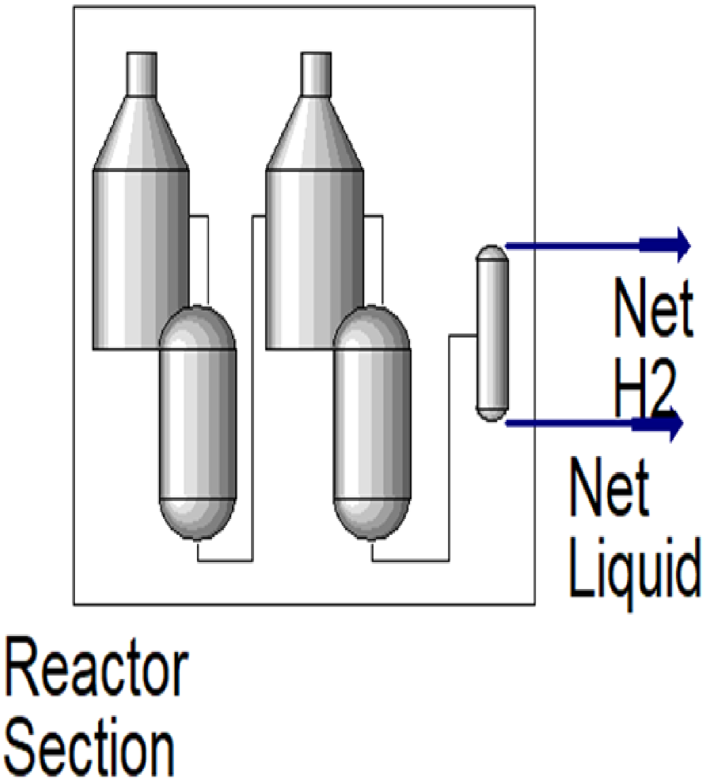


Figure: 3.2. Continuous Catalytic Reformer (CCR)

Table: 3.9 Material Balance of Continuous Catalytic Reformer :

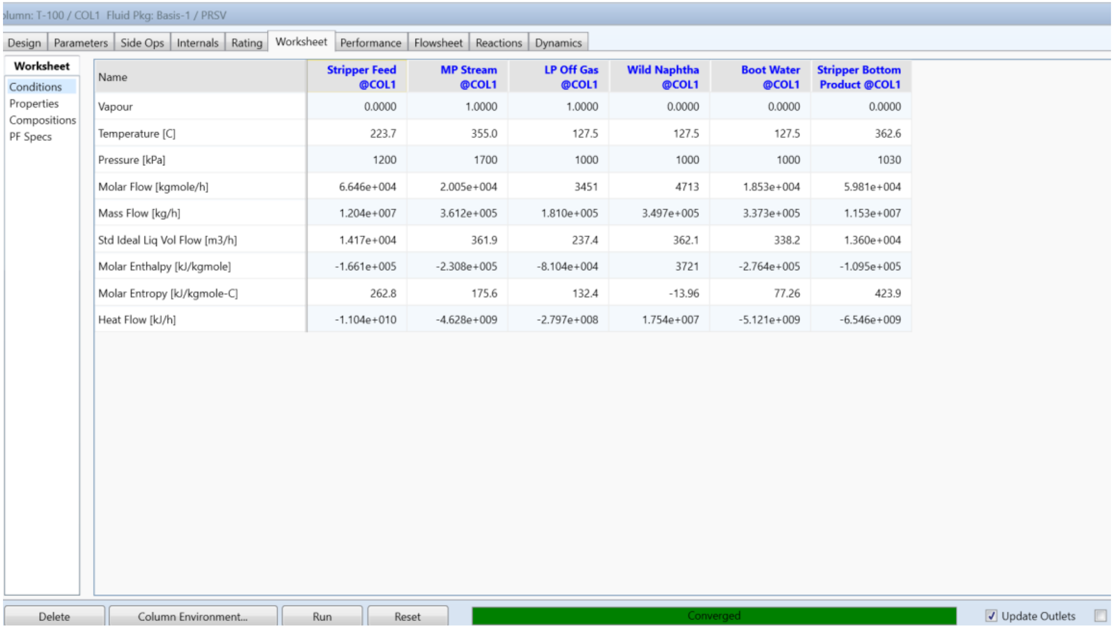
Stream No:	**1**		**2**		**3**		**4**	
Stream name	**Reformer feed**		**Reformate products**		**Hydrogen rich gas**		**LPG**	
Composition	**wt%**	**Kg/h**	**SOL wt%**	**EOL Kg/h**	**SOL wt%**	**EOL wt%**	**SOL wt%**	**EOL wt%**
H2	-	-	-	-	92.7	91.0	-	-
C1	-	-	-	-	2.1	2.7	-	-

C2	-	-	-	-	1.3	1.7	5.6	5.4
C3	-	-	-	-	1.3	1.7	26.6	24.8
C4	-	-	-	-	1.3	1.6	66.9	68.9
C5+	4.11	1902.8	-	-	1.3	1.3	0.9	0.9
C6	11.34	5249.9	-	-	-	-	-	-
C7	19.03	8810.2	-	-	-	-	-	-
C8	26.32	12185.2	-	-	-	-	-	-
C9	23.82	11027.8	-	-	-	-	-	-
C10	12.05	5578.7	-	-	-	-	-	-
C11+	3.33	1541.7	-	-	-	-	-	-
Total	**100.0**	**46296.3**	**44082**	**-**	**100.0**	**100.0**	**100.0**	**100.0**
Flowrate (kg/h)	46296.3		44082	43379	-	4471	1157	1615
Spgr	0.725		0.796		-		0.536	0.538

Chapter 4

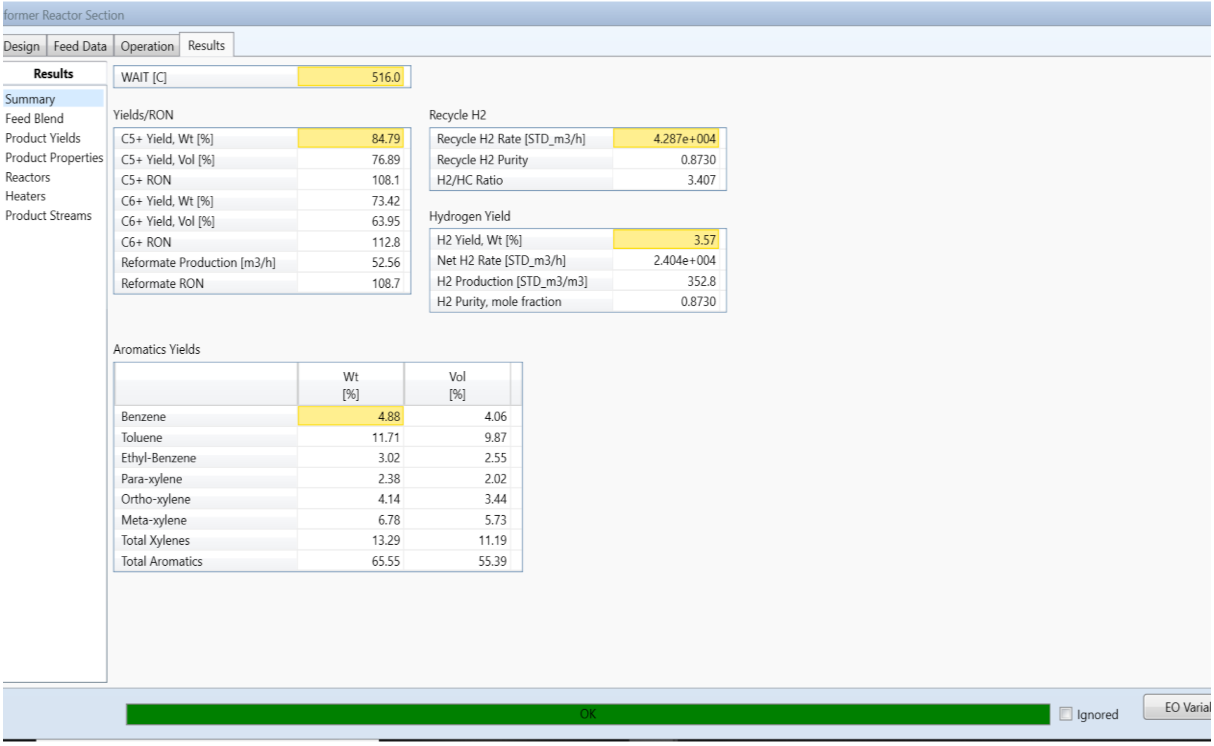
4. Result and Discussion:

4.1. Simulation result:



Name	Stripper Feed @COL1	MP Stream @COL1	LP Off Gas @COL1	Wild Naphtha @COL1	Boot Water @COL1	Stripper Bottom Product @COL1
Vapour	0.0000	1.0000	1.0000	0.0000	0.0000	0.0000
Temperature [C]	223.7	355.0	127.5	127.5	127.5	362.6
Pressure [kPa]	1200	1700	1000	1000	1000	1030
Molar Flow [kgmole/h]	6.646e+004	2.005e+004	3451	4713	1.853e+004	5.981e+004
Mass Flow [kg/h]	1.204e+007	3.612e+005	1.810e+005	3.497e+005	3.373e+005	1.153e+007
Std Ideal Liq Vol Flow [m3/h]	1.417e+004	361.9	237.4	362.1	338.2	1.360e+004
Molar Enthalpy [kJ/kgmole]	-1.661e+005	-2.308e+005	-8.104e+004	3721	-2.764e+005	-1.095e+005
Molar Entropy [kJ/kgmole-C]	262.8	175.6	132.4	-13.96	77.26	423.9
Heat Flow [kJ/h]	-1.104e+010	-4.628e+009	-2.797e+008	1.754e+007	-5.121e+009	-6.546e+009

Figure: 4.1. Final products of DHT.



former Reactor Section

Design | Feed Data | Operation | Results

Results

Summary
Feed Blend
Product Yields
Product Properties
Reactors
Heaters
Product Streams

WAIT [C]	516.0

Yields/RON

C5+ Yield, Wt [%]	84.79
C5+ Yield, Vol [%]	76.89
C5+ RON	108.1
C6+ Yield, Wt [%]	73.42
C6+ Yield, Vol [%]	63.95
C6+ RON	112.8
Reformate Production [m3/h]	52.56
Reformate RON	108.7

Recycle H2

Recycle H2 Rate [STD_m3/h]	4.287e+004
Recycle H2 Purity	0.8730
H2/HC Ratio	3.407

Hydrogen Yield

H2 Yield, Wt [%]	3.57
Net H2 Rate [STD_m3/h]	2.404e+004
H2 Production [STD_m3/m3]	352.8
H2 Purity, mole fraction	0.8730

Aromatics Yields

	Wt [%]	Vol [%]
Benzene	4.88	4.06
Toluene	11.71	9.87
Ethyl-Benzene	3.02	2.55
Para-xylene	2.38	2.02
Ortho-xylene	4.14	3.44
Meta-xylene	6.78	5.73
Total Xylenes	13.29	11.19
Total Aromatics	65.55	55.39

OK
Ignored
EO Varial

Figure:4.4. Final products of CCR

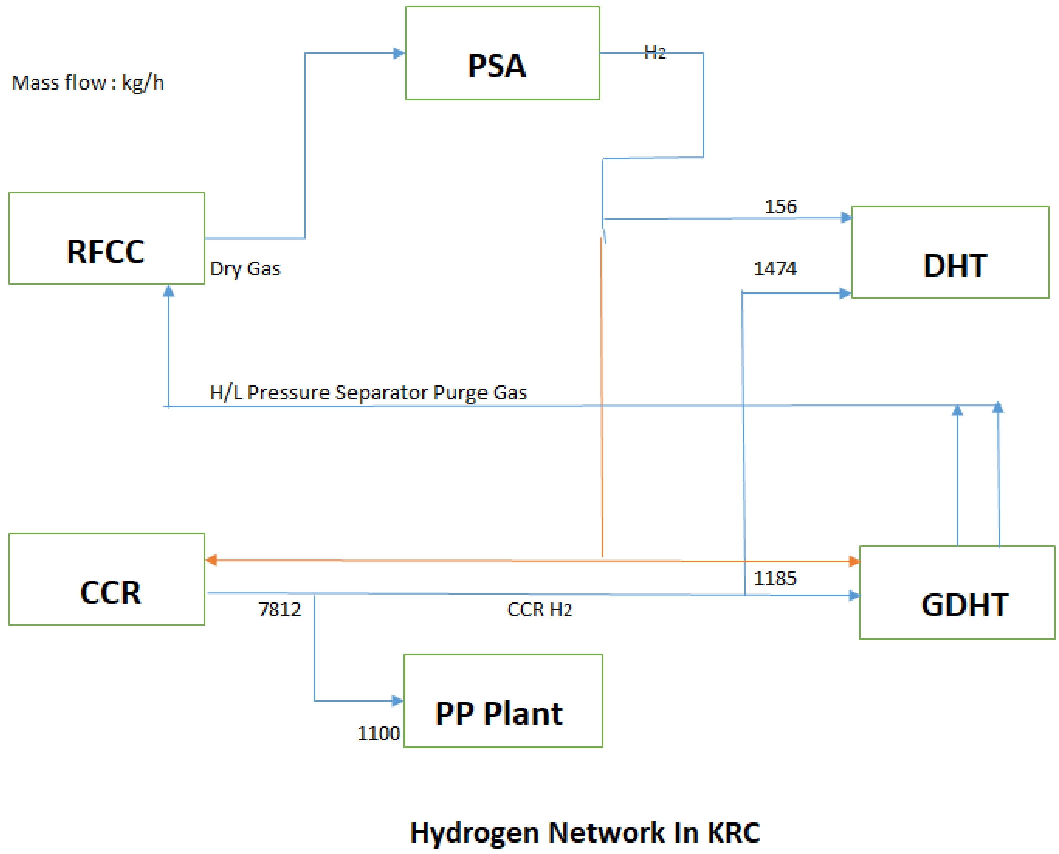


Figure:4.5. Hydrogen Network in KRC

4.2. Discussion:

The hydrogen has been managed by making a balance for all units that producing and consuming hydrogen in the above network in order to achieve the international standard specification of gasoline octane number the impurities have been reduced to minimum quantity.

Hydrogen produce from CCR unit is 7812 kg/h, hydrotreating units (DHT & GDHT) consumed 2659 kg/h and 1100 kg/h transferred in batches to pp plant, the remained amount 4053 kg/h is excess which can be used for utilities in the refinery (furnace fuel and electricity) or other choice sell it in the market which achieve more revenue to the company.

Chapter 5

5. Conclusion and Recommendation:

5.1. Conclusion:

1. Refineries have a number of different options to consider in addressing the demand for additional hydrogen to increase the quality of products, reducing the impurities and utilize the operation units.

2. This study apply material balance and Excel sheet to manage the hydrogen in (PSA, DHT, GDHT&CCR) units.

3. This study increase the RON of gasoline from 98 to 108, moreover increase production of gasoline to cover local need of gasoline and have surplus in hydrogen which can gain hard currency for the refinery.

5.2. Recommendations for Future Work:

The following suggestions for future work can be considered:

- Developed a new model to produce hydrogen by steam reforming of methane (SMR) because it is most widely used and cheapest method.
- Applying electrolysis of water technology which has low cost, high hydrogen purity and higher flexiblity and reactivity in the operation of the device.

5.3. Reference:

1. Hydrogen the fuel for 21st century.

2. https://courses.lumenlearning.com(July 2021).

3. (Hydrogen Applications in industry –WHA International, Inc <https://wha-international.com/hydrogen-in-industry/>).

4. (U.S. refinery demand for hydrogen (2008-14).

5. (Int . J. Process Systems Engineering. Vol. 1, Nos. 3/4, 2011).

6. (20th Annual International Pittsburgh Coal Conference September 15-19, 2003 Pittsburgh, PA).

7. (Yang 2008).

8. (E. Bonabeau et al.,, 1999).

9. (Ancheyta-Juarez J et al.,, 2000).

10. (D'Ippolito SA et al.,, 2008).

11. (Donald, M. L et al, 1985).

12. PSA manual 2018.

13. DHT last version manual 2018.

14. CCR manual 2006.