INTERNSHIP REPORT

OSIP-2024

Online Internship Programme (OIP-2024)

Internship Report

On

Petroleum Refinery Engineering

By:

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BIRLA INSTITUTE OF TECHNOLOGY, MESRA

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Indian Institute of Chemical Engineers (IIChE)

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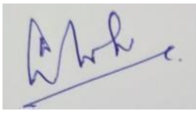
OSIP-2024

Certificate from the IIChE

This is to certify that Mr. AMARTYA ABHYANKAR of BIRLA INSTITUTE OF TECHNOLOGY, MESRA has successfully completed online summer internship programme in our organization. The matter embodied in this report is a genuine to the best of our knowledge and belief and has not been submitted before, neither to this Institute nor to any other organization for the fulfilment of the requirement of any course of study. During his internship tenure in IIChE, we found him as a hard working, sincere, and diligent person and his behaviour and conduct was good. We wish him all the best for his future endeavour.

This project report is required to validate with original certificate of completion.



Convener, OSIP-2024

Acknowledgement

I would like to express my deepest gratitude towards Indian Institute of Chemical Engineers (IIChE) for providing me the opportunity to become a part of the Online Summer Internship Programme , 2024 and for giving me a platform to learn about Petroleum Refinery Engineering as well as many aspects and areas of Chemical Engineering. The internship not only enhanced my knowledge but also helped me to relate the subject in accordance to the industries and made me get a closer look at it. It was a very engaging and meaningful learning opputunity for me and I, hereby, thank my couse instructor and guide, Mr. Kisalay Kumar , who not only presented the subject in a very interactive manner but also cleared our doubts effectively.

Finally, I would like to thank all the respected aurthorities of IIChE as well as the esteemed webinar guest speakers for providing such a beneficial insight in the area of Chemical Engineering.

Preface

Objectives of Online Internship Program

- Assist the student's development of employer-valued skills such as teamwork, communications and attention to learn Engineer’s responsibilities and ethics.
- Enhance and/or expand the student's knowledge of a particular area(s) of skill.
- Expose the student to professional role models or mentors who will provide the student with support in the early stages of the internship and provide an example of the behaviours expected in the intern's workplace.
- To familiarize with various materials, processes, products and their applications along with relevant aspects of technology and troubleshooting.
- To gain experience in writing technical report/project.

Course Outcome

- The basic idea of different real life industrial problems, trouble shooting, decision making and preventive maintenance techniques and professional culture of industry, work ethics and attitudes in industry. The different live situation, trouble shooting and modern technological application.
- Course materials to be provided to the students for reference (in PDF format). The study material will be shared with the students through IIChE for its record.
- Assignment will be given for the solution / conceptual idea and which may be discussed during the tutorial class.
- Mini project will be given for developing their analytical ability which helps them to realize the value of practical training.
- Importance will be given on the application of modern tools for the industrial automation / up-gradation / scale-up.
- Conceptual theory for the regular class room discussion and its application is real-life industrial problem resolution.
- Case studies based on real life application.

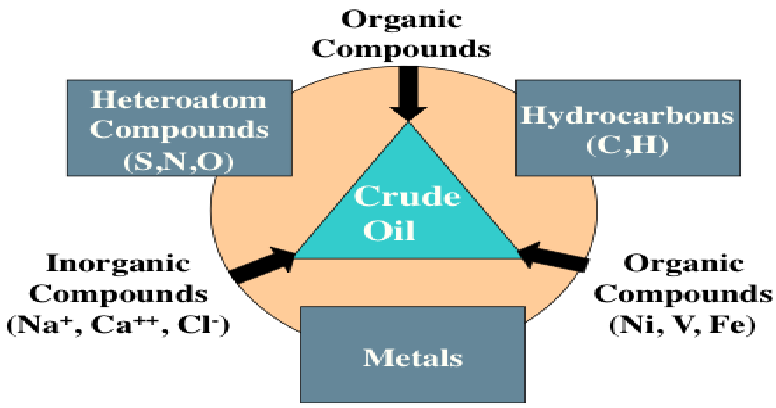
1. Introduction: Overview of the Industry

Petroleum and derivatives such as asphalt have been known and used for almost 6000 years and there is evidence of use of asphalt in building more than 600 years ago. Modern petroleum refining began in 1859 with discovery of petroleum in Pennsylvania and subsequent commercialization.

Oil and gas production includes exploration, drilling, extraction, stabilization. The underground traps of oil and gas are called reservoir. Various types of traps are structural traps, stratigraphic traps and combination traps Most reservoir contain water also along with oil and gas. Reserves are classified as proven, probable and possible reserves. Earlier finding of oil and gas was matter of luck and hit and miss process.

COMPOSITION OF PETROLEUM (CRUDE OIL):-

Petroleum (Crude oil) consists of mainly carbon (83-87%) and hydrogen (12-14%) having complex hydrocarbon mixture like paraffins, naphthenes, aromatic hydrocarbons, gaseous hydrocarbons (from CH4 to C4H10). Besides crude oil also contains small amount of non hydrocarbons (sulphur compounds, nitrogen compounds, oxygen compounds) and minerals heavier crudes contains higher sulphur.



Depending on predominance of hydrocarbons, petroleum is classified as paraffin base, intermediate base or naphthenic base-

Hydrocarbons

Hydrogen Family	Distinguishing characteristics	Major hydrocarbons	Remarks
Paraffins (Alkanes)	Straight carbon chain	Methane, ethane, propane, butane, pentane, hexane	General formula C_nH_{2n+2} Boiling point increases as the number of carbon atom increases. With number of carbon 25-40, paraffin becomes waxy.
Isoparaffins (Iso alkanes)	Branched carbon chain	Isobutane, Isopentane, Neopentane, Isooctane	The number of possible isomers increases as in geometric progression as the number of carbon atoms increases.
Olefins (Alkenes)	One pair of carbon atoms	Ethylene, Propylene	General formula C_nH_{2n} Olefins are not present in crude oil, but are formed during process. Undesirable in the finished product because of their high reactivity. Low molecular weight olefins have good antiknock properties.
Naphthenes	5 or 6 carbon atoms in ring	Cyclopentane, Methyl cyclopentane, Dimethyl cyclopentane, cyclohexane, 1,2 dimethyl cyclohexane.	General formula C_nH_{2n+2}-$2R_n$ R_N is number of naphthenic ring The average crude oil contains about 50% by weight naphthenes. Naphthenes are modestly good components of gasoline.
Aromatics	6 carbon atom in ring with three around linkage.	Benzene, Toluene, Xylene, Ethyl Benzene, Cumene, Naphthaline	Aromatics are not desirable in kerosene and lubricating oil. Benzene is carcinogenic and hence undesirable part of gasoline.

Non Hydrocarbons

Non-hydrocarbons	Compounds	Remarks
Sulphur compounds	Hydrogen sulphide, Mercaptans	Undesirable due to foul odour 0.5% to 7%
Nitrogen compounds	Quinotine, Pyradine, pyrrole, indole, carbazole	The presence of nitrogen compounds in gasoline and kerosene degrades the colour of product on exposure to sunlight. They may cause gum formation normally less than 0.2.
Oxygen compounds	Naphthenic acids, phenols	Content traces to 2%. These acids cause corrosion problem at various stages of processing and pollution problem.

REFINERY PROCESSES:-

Refining of crude oils or petroleum essentially consists of primary separation processes and secondary conversion processes. The petroleum refining process is the separation of the different hydrocarbons present in the crude oil into useful fractions and the conversion of some of the hydrocarbons into products having higher quality performance. Atmospheric and vacuum distillation of crude oils is the main primary separation processes producing various straight run products, e.g., gasoline to lube oils/vacuum gas oils (VGO). These products, particularly the light and middle distillates, i.e., gasoline, kerosene and diesel are more in demand than their direct availability from crude oils, all over the world. The typical refinery operation involves separation processes, conversion processes, finishing processes, environmental protection processes.

SEPARATION PROCESSES

- Distillation
- Absorption
- Extraction
- Crystallisation
- Adsorption

PRIMARY DISTILATION (Atmospheric Distillation)

- Refinery gases
- Liquefied petroleum gases

- Gasolines or naphtha (light/heavy)
- Kerosene, lamp oil jet fuel

- Diesel oil and domestic heating oils
- Heavy Industrial fuels

SECONDARY DISLLATION (Vacuum Distillation)

- Light Distillate
- Middle distillate
- Heavy distillate • Asphalt/bitumen

CONVERSION PROCESSES

Process for Improvement of Properties

- Catalytic reforming
- Isomerisation
- Alkylation

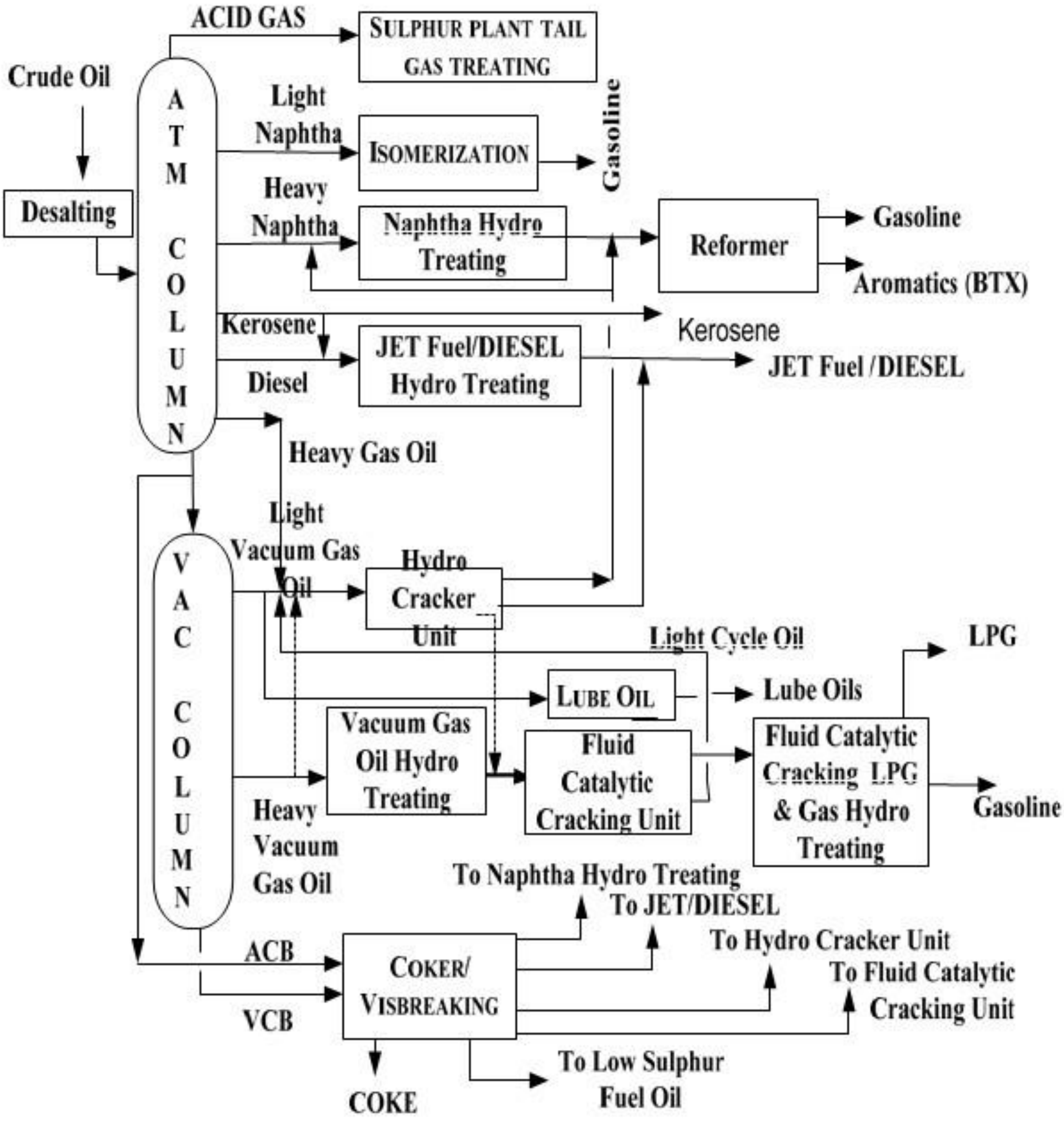


Figure: Typical Refinery Processes and Products

Thermal processes:

- Visbreaking
- Coking

Catalytic Processes

- Catalytic cracking(FCC)
- Hydrocracking
- Steam reforming
- Hydroconversion

FINISHING PROCESSES

- Hydrotreatment/hydrogenation
- Sweetening

ENVIRONMENTAL PROTECTION PROCESSES

- Acid gas processing
- Stack gas processing
- Waste water treatment process

TYPES OF PETROLEUM REFINING PROCESSES

PRIMARY PROCESSES: Separating crude into its various fractions e.g. CDU/VDU

SECONDARY PROCESSES: Processing residues from primary processes and upgrading them to distillates e.g. FCCU, HCU

RESIDUE UPGRADATION PROCESSES: Bottom of the barrel upgradation eg. RFCCU, DCU, DCC

FINISHING/ PRODUCT QUALITY IMPROVEMENT PROCESSES: Processes to improve product quality and meet stringent product quality specifications eg. DHDS, DHDT, CRU.

MAXIMIZING VALUE ADDITION TO REFINERY STREAMS:-

For a refinery to be successful today, it has to be integrated with petrochemical to benefit from better realization from value added products and to mitigate the effect of volatile oil process and highly competitive refining business. Some of the streams which can maximize value addition to the refinery is given-

Table: Maximizing Value Addition to Refinery Streams

Streams	Utilization
Fuel Gas	H_2
FCC	
Ethylene	Ethyl Benzene to Styrene
Propylene	Cumene, Iso-Propanol
Butylene	Methyl Ethyl Keton, MTBE, Xylenes
C_3	Propylene + H_2
C_4	Discussed Separately
LPG	BTX
C_5	TAME
Light naphtha	LPG, BTX
Heavy Naphtha	Aromatics
Kerosene	n-paraffins to LAB
LCO (FCC unit)	Mixed Naphthalenes
Coker Kerosene	α-Olefins

2. Discussion on different industrial application

Refining of crude oils or petroleum essentially consists of primary separation processes and secondary conversion processes. The petroleum refining process is the separation of the different hydrocarbons present in the crude oil into useful fractions and the conversion of some of the hydrocarbons into products having higher quality performance. Atmospheric and vacuum distillation of crude oils is the main primary separation processes producing various straight run products, e.g., gasoline to lube oils/vacuum gas oils (VGO).

PRETREATMENT OF CRUDE OILS

Crude oil comes from the ground, which contains variety of substances like gases, water, dirt (minerals) etc. Pretreatment of the crude oil is important if the crude oil is to be transported effectively and to be processed without causing fouling and corrosion in the subsequent operation starting from distillation, catalytic reforming and secondary conversion processes.

CRUDE DESALTING

It is a water washing operation performed at the refinery site to get additional crude oil clean up. Crude Oil Desalting consists of Purifying process Remove salts, inorganic particles and residual water from crude oil Reduces corrosion and fouling Desalting process is used for removal of the salts, like chlorides of calcium, magnesium and sodium and other impurities as these are corrosive in nature. The crude oil coming from field separator will continue to have some water/brine and dirt entrained with it. Water washing removes much of the watersoluble minerals and entrained solids (impurities). There are two types of desalting: single & multistage desalting. Commercial crudes, salt contents 10-200 ppb, earlier 10-20 ppb were considered satisfactorily low. However, many refiners now aim at 5 ppb or less (1-2 ppb) which is not possible through single stage desalting, hence two stage desalting is required

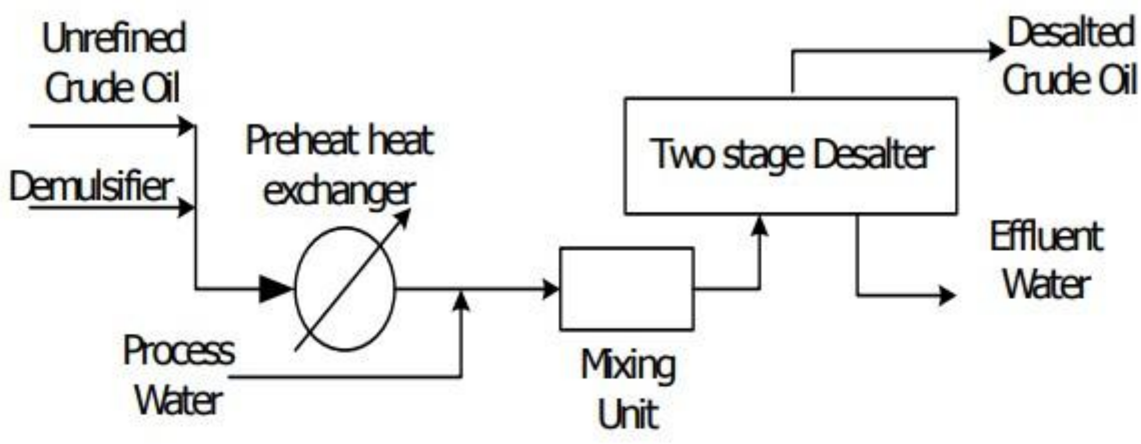


Figure- Crude oil Desalting

CRUDE OIL DISTILLATION

Desalted crude flows to atmospheric and vacuum distillation through crude pre flashing section. Atmospheric distillation column (ADU) and Vacuum distillation column (VDU) are the main primary separation processes producing various straight run products, e.g., gasoline to lube oils/vacuum gas oils (VGO). These products, particularly the light and middle distillates, i.e., gasoline, kerosene and diesel are more in demand than their direct availability from crude oils, all over the world.

Two stage Desalter Desalted Crude Oil Effluent Water Process Water Unrefined Crude Oil Demulsifier Preheat heat exchanger Mixing Unit 204 Crude oil distillation consists of atmospheric and vacuum distillation. The heavier fraction of crude oil obtained from atmospheric column requires high temperature. In order to avoid cracking at higher temperature the heavier fraction are fractionated under vacuum. Typical flow diagram of crude oil distillation is given .

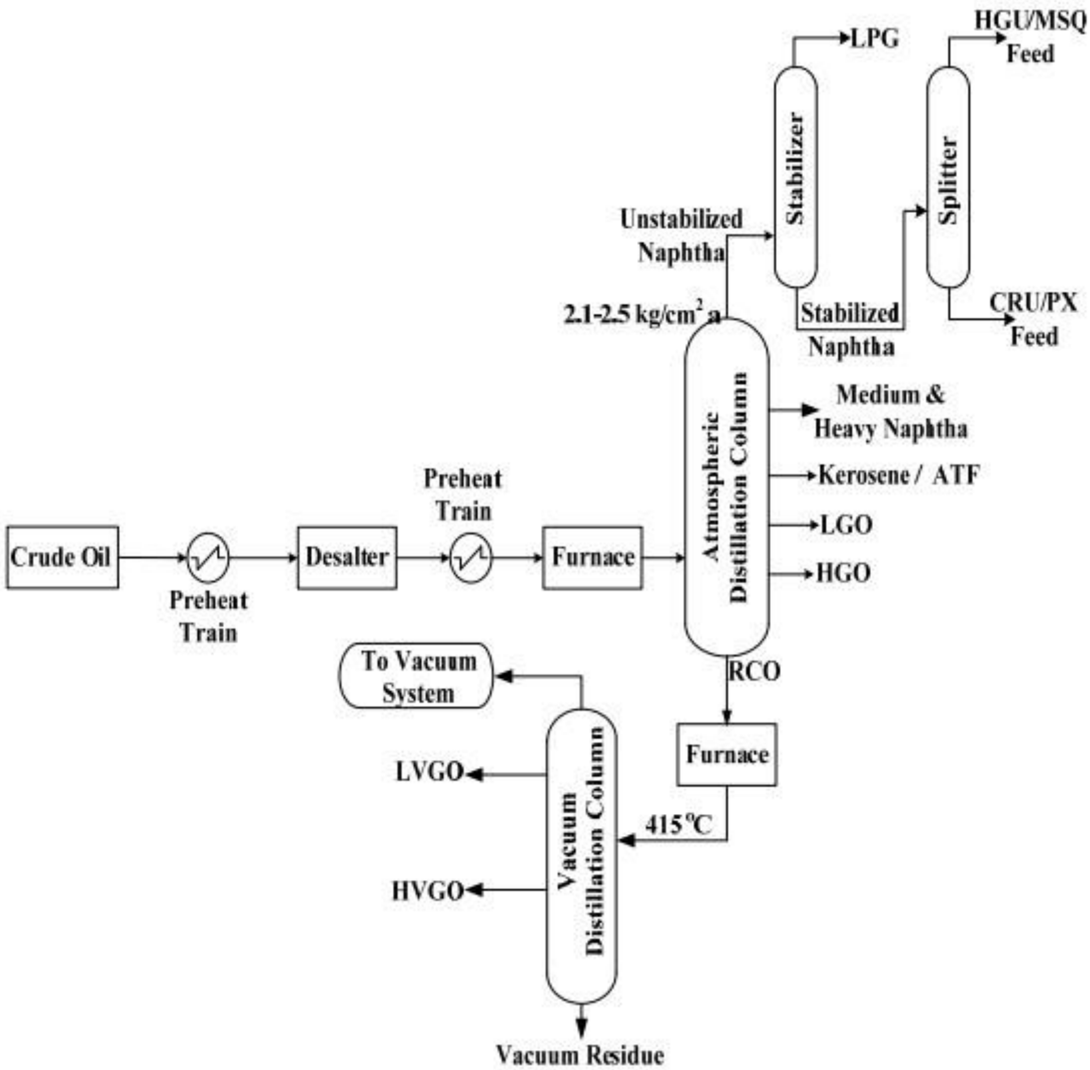


Figure: Atmospheric and Vacuum Crude oil distillation

Column	Fraction	Temperature	Carbon range	Uses
Atmospheric column	Fuel Gases	>40	C_1-C_2	Fuel
	LPG		C_3-C_4	Domestic fuel
	Straight run gasoline/	20-90	C6-C10	Gasoline pool
	Naphtha (Medium and heavy)	130-180	C6-C10	Catalytic reforming and aromatic plant feed stock Steam cracker, synthesis gas manufacture
	Kerosene	150-270	C11-12	Aviation turbine fuel, Domestic fuel, LAB feed stock (paraffin source)
	Light gas oil	230-320	C13-C17	High speed diesel component
	Heavy gas oil	320-380	C18-C25	High speed diesel component
Vacuum column	Light vacuum gas oil	370-425	C18-C25	Feed to FCC /HCU
	Heavy vacuum gas oil	425-550	C26-C38	Feed to FCC /HCU
	Vacuum slop	550-560		RFCCU feed
	Vacuum Residue	>560	>C38	Bitumen/ Visbreaker feed

Table: Various Streams From Atmospheric And Vacuum Distillation Column

ATMOSPHERIC COLUMN:

Various steps in atmospheric crude oil distillation are Preheating of Desalted crude Preflash Distillation Stabilization of Naphtha The desalted crude oil from the second stage desalting process is heated in two parallel heat exchanger. The preheated crude having temperature of about 180o C is goes to pre flash drum where about 3-4percent of light ends are removed. The preheated crude from the preheater section is further 206 heated and partially vaporized in the furnace containing tubular heater. The furnace has two zones: radiant section and convection section. The radiant zone forms the combustion zone and contains the burners. In convection zone the crude is further heated (inside the tube) by the hot flue gases from the radiant section.

PRODUCTS of ADU:

Major product from atmospheric column are light gases and LPG, light naphtha,medium naphtha,heavy naphtha,kerosene,gas Oil(diesel),atmospheric residue. Unstabilized Naphtha consists of LPG, naphtha and light gases (C-5 115 o C) Intermediate Naphtha (Bombay High) (135o C) Solvent Naphtha Heavy Naphtha (130-150 o C) routed to diesel or naphtha. Kero/ATF (140-270/250o C) Light Gas Oil (250/270-320o C) Heavy Gas Oil (320-380o C) Reduced Crude Oil.

VACUUM DISTILLATION COLUMN (VDU)

The bottom product also called reduced crude oil, from the atmospheric column is fractionated in the vacuum column. Reduced crude oil is very heavy compared to crude oil distilling under pressure requires high temperature. Distillation under vacuum permits fractionation at lower temperature which 207 avoid cracking of the reduced crude oil and coking of the furnace tube. Vacuum is maintained using three stage steam ejector. The reduced crude oil from atmospheric column at about 360o C is heated and partially vaporized in the furnace

PRODUCTS FROM VDU:

Various products from VDU areLight gasoil, Heavy gas oil, light lube distillate, medium lube distillate, heavy lube distillate and vacuum column residue

OPERATING PRESSURE OF VACUUM COLUMN:

About 90-95 mm Hg at the top and About 135-140 mm Hg at the bottom

CRACKING

Cracking of heavy residue is most commonly used method for upgradation of residues. This involves of decomposition of heavy residues by exposure to extreme temperatures in the presence or absence of catalysts.

THERMAL CRACKING:Cracking at elevated temperatures in the absence of catalyst eg: Visbreaking, delayed coking, Fluid coking etc.

CATALYTIC CRACKING: Cracking in presence of catalyst eg: FCC , Hydrocracking, DCC

Delayed Coking and Visbreaking	Technology for the bottom of the barrel upgradation; means of disposing of low value resids by converting part of the resids to more valuable liquid and gas products.
Uniflex Technology:	Technology for processing low quality residue by thermal cracking to produce high quality distillate products.
Fluidized Catalytic Cracking (FCC) and Residual Fluidized Catalytic Cracking (RFCC)	A technology introduced to contain generation of black oil from refinery and to increase the production of high value products like LPG, MS and Diesel.
Hydrocracking	Processes for Residue up gradation FCC process, delayed coking process &visbreaking
Deep Catalytic Cracking (DCC) and IOCL's INDMAX	For selectively cracking feed stocks to light olefins.

Table: Residue Upgradation Technologies in Refineries

Table : Various Thermal Cracking Process

Process	Process conditions
Visbreaking	Mild thermal cracking (low severity) Mild (470-500°C) heating at 50-200 psig Improve the viscosity of fuel oil Low conversion (10%) to 430^{0}F Residence time1-3 min Heated coil or drum
Delayed coking	Operates in semi batch mode Moderate (900-960°F) heating at 90 psig Soak drums (845-900°F) coke walls
	Coked until drum solid Coke (removed hydraulically) 20-40% on feed, Yield 430^{0}F, 30%
Fluid Coking	Server (510-520°C) heating at 10 psig Oil contact refractory coke Bed fluidized with steam-even heating, Higher yield of light ends (<Cs),Less coke yield
Flexicoking	A continuous fluidised bed technology which converts heavy residue to lighter more valuable product. The process essentially eliminates the coke production. Temperature 525°C

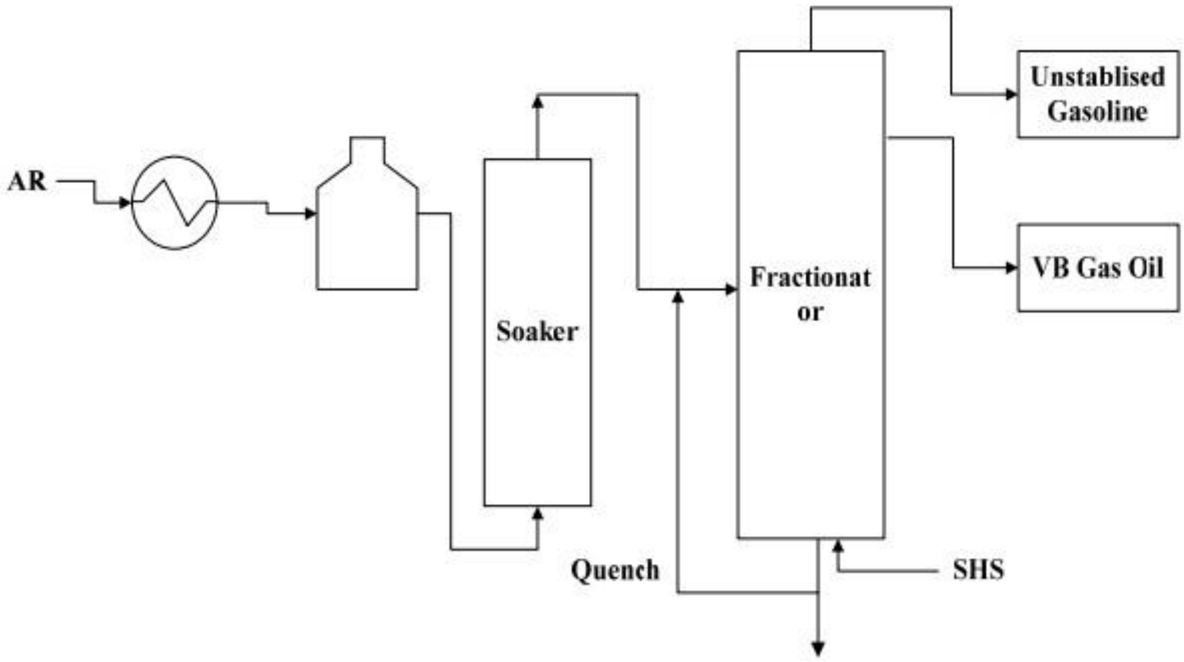


Figure: Visbreaking with Soaker

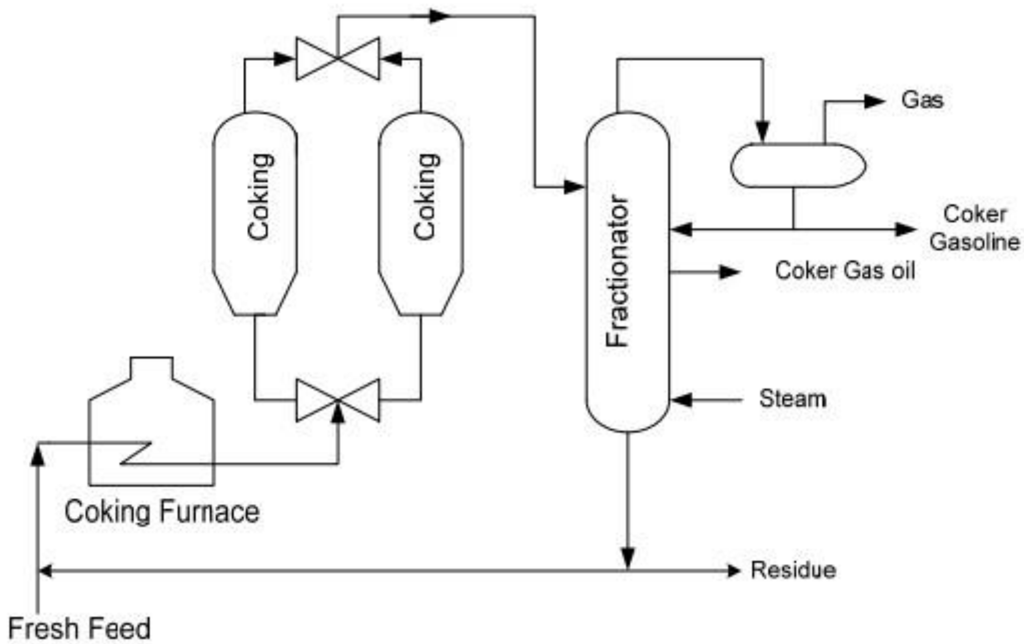


Figure: Process Flow Chart of Delayed Coking

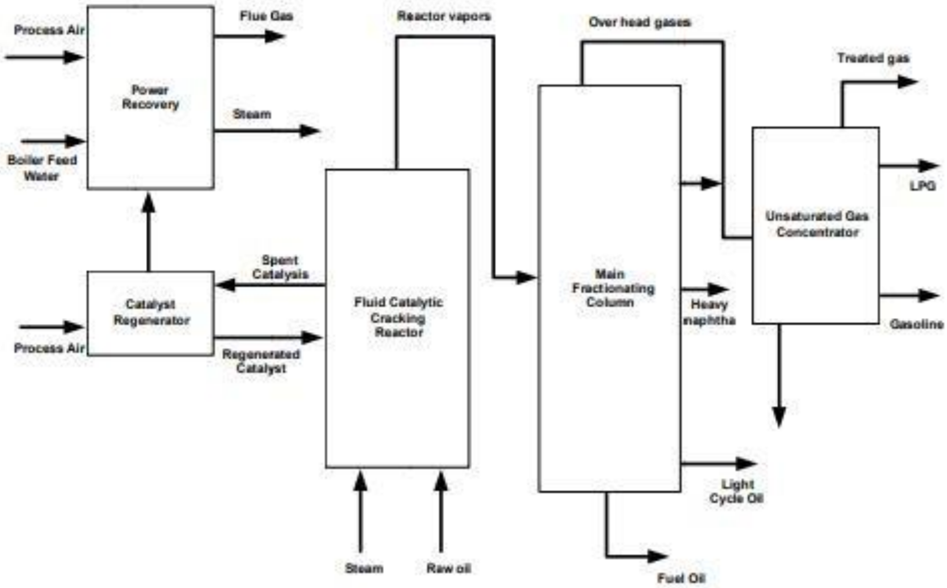
CATALYTIC CRACKING

Catalytic cracking process was developed in1920 by Eugene Houdry for upgradation of residue was commercialized latter in 1930. Houdry process was based on cyclic fixed bed configuration. There has been continuous upgradation in catalytic in catalytic cracking process from its incept of fixed bed technology to latter fluidized bed catalytic cracking (FCC).The feed stock for catalytic cracking is normally light gas oil from vacuum distillation column. Catalytic cracking cracks low value high molecular weight hydrocarbons to more value added products (low molecular weight) like gasoline, LPG Diesel along with very important petrochemical feedstock like propylene, C4 gases like isobutylene, Isobutane, butane and butane.

Main reactions involved in catalytic cracking are

Cracking Isomerisation Dehydrogenenation Hydrogen transfer Cyclization Condensation Alkylation and dealkylation

Paraffins	**Cracking → Paraffins + Olefins**
Olefins	**Cracking → LPG Olefins** **Cyclization → Naphthenes**
	Isomerization → Branched Olefins → H Transfer → Branched Paraffins **H Transfer → Paraffins** **Cyclization → Coke** **Condensation → Coke** **Dehydrogenation → Coke**
Naphthenes	**Cracking → Olefins** **Dehydrogenation → Cyclo-Olefins → Dehydrogenation → Aromatics** **Isomerization → Naphthenes with different rings**
Aromatics	**Side chain cracking → Unsubstituted aromatics + Olefins** **Trans alkylation → Different alkyl aromatics** **Dehydrogenation → Polyaromatics → Alkylation Dehydrogenation Condensation → Coke**
Hydrogen Transfer → Naphthene + Olefin → Aromatic + Paraffin	



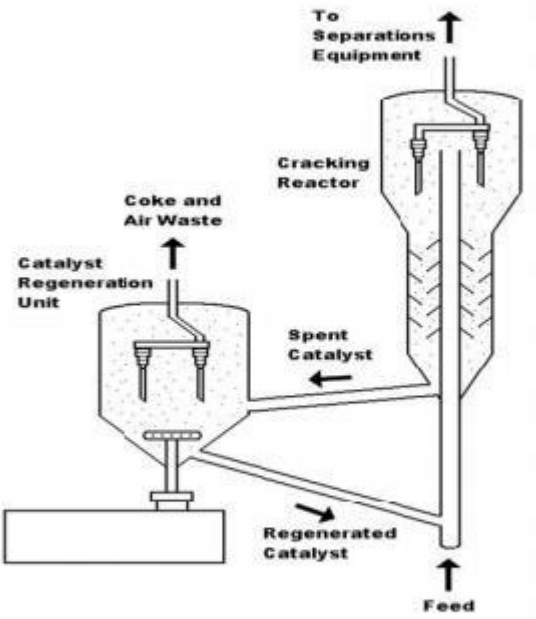


Figure: Fluid Catalytic Cracking Process and FCC Reactor

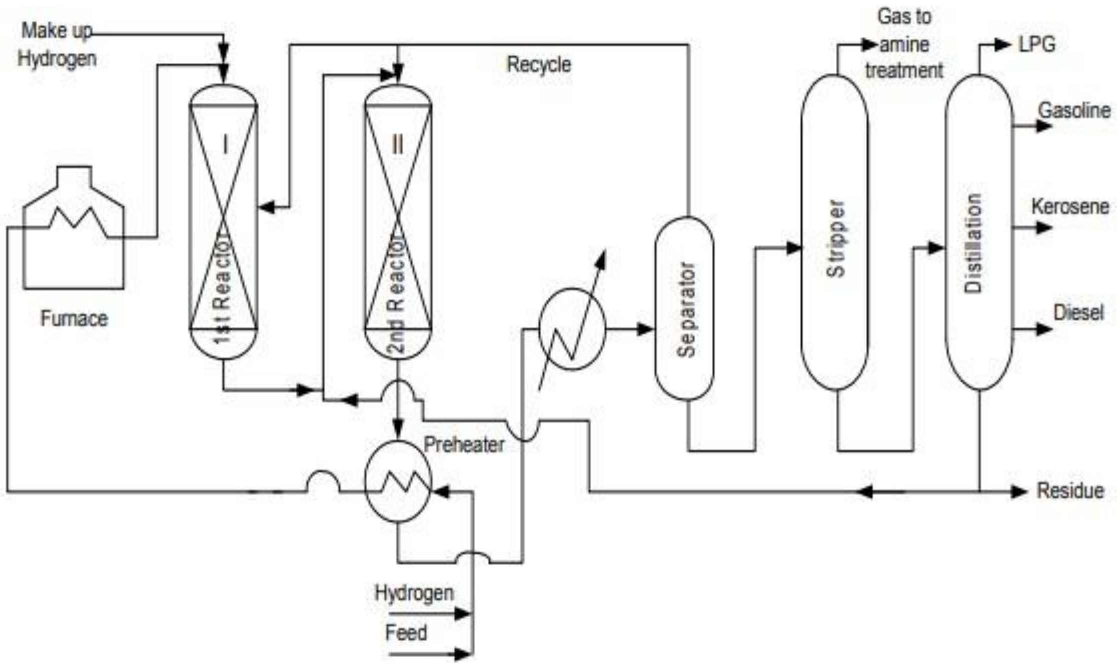


Figure: Hydrocracking

CATALYST DEACTIVATION

Catalyst activation may occur due to coke deposition and metal accumulation. Coke Depositions may be due to condensation of poly-nuclear and olefinic compounds into high molecular weight which cover active sites. Metal Accumulation occurs at the pore entrances or near the outer surface of the catalyst.

CATALYST REGENERATION

Catalyst regeneration is done by burning off the carbon, and sulphur and circulation of circulate nitrogen with the recycle compressor, injecting a small quantity of air and maintaining catalyst temperature above the coke ignition temperature.

3. Case study analysis

The petroleum industry began with the successful drilling of the first commercial oil well in 1859, and the opening of the first refinery two years later to process the crude into kerosene. To those unfamiliar with the industry, petroleum refineries may appear to be complex and confusing places. Refining is the processing of one complex mixture of hydrocarbons into a number of other complex mixtures of hydrocarbons.

HISTORICAL.

In the United States, Indians used oil seepages in Pennsylvania as medicines, and worldwide, various bitumens were known in Biblical times. Moses' burning bush may well have been an accidentally ignited gas vent. Drake's crude oil well, completed in 1859, showed the world the existence of extensive underground reservoirs of material then mainly Useful as a source of kerosene for illuminating lamps. The useless gasoline, which at times had been towed out to sea and burned as a nuisance, gradually became the major product with demand exceeding the supply. Improved quality, as represented by antiknock value, was also desired. The available quantity was extended by converting less desirable fractions into gasoline, first by thermal, later by catalytic cracking processes. Quality improvement in gasoline was brought about by cracking, the tetraethyllead antiknock properties discovery, polymerization, alkylation, aromatization, and through the gradual awareness that transformations of many kinds were possible by the application of organic processes on a large scale. Refining has always been pushed along reluctantly by economic factors. For years, many companies viewed refining as a necessary evil to be endured so that they could 2 make money from the more. vital production and sale of the crude oil which they produced. Only recently, most companies have come to realize that their purpose is to take a many-component raw material and convert it, at maximum profit, into materials to fulfill the needs of a complex and constantly shifting multiproduct market. In 1930, a company could market only gasoline, kerosene, heating fuel, gas oil, and residuum and show a profit. Today the market is far more complicated, and the marketing decisions are more difficult. Simple fractionation of crude oil Into fractions was once sufficient but such simple products would rarely be salable now. Quality needs require upgrading, blending, and consistent quality control of the finished products, although the crudes refined may vary greatly in type and distillate content.

TABLE TYPICAL APPROXIMATE CHARACTERISTICS AND PROPERTIES AND GASOLINE POTENTIAL OF VARIOUS CRUDES (Representative average numbers)

Crude source	Paraffins (% vol)	Aromatics (% vol)	Naphthenes (% vol)	Sulfur (% wt)	API gravity (approx.)	Napht. yield (% vol)	Octane no (typical)
Nigerian -Light	37	9	54	0.2	36	28	60
Saudi -Light	63	19	18	2	34	22	40
Saudi -Heavy	60	15	25	2.1	28	23	35
Venezuela -Heavy	35	12	53	2.3	30	2	60
Venezuela -Light	52	14	34	1.5	24	18	50
USA -Midcont. Sweet	-	-	-	0.4	40	-	-
USA -W. Texas Sour	46	22	32	1.9	32	33	55
North Sea -Brent	50	16	34	0.4	37	31	50

Top petroleum-producing countries

#	Producing Nation for 2004	(×106bbl/d)	(×103/d)
1	**Saudi Arabia**	10.37	1,649
2	**Russia**	9.27	1,474
3	**United states 1**	8.69	1,382
4	**Iran (OPEC)**	4.09	650

REFINERIES IN INDIA

1.**Barauni Refinery** in Eastern India was built in collaboration with the at a cost of Rs.49.4 crores and went on stream in July, 1964. By November, 1967, the initial capacity of 2 MMTPA was expanded to 3 MMTPA by 1969. The present capacity of this refineries is 6.00 MMTPA. A Catalytic Reformer Unit (CRU) was also added to the in 1997 for production of unleaded. Projects are also planned for meeting future fuel quality requirements.

2.**Bongaigaon Refinery & Petrochemicals Limited (BRPL)** has the unique distinction of being the first indigenous grass root Refinery in the country integrated with a Petrochemical complex at one location.At present, the Refinery is processing crude available from the oil fields of East India and Ravva crude oil from the Krishna-Godavari basin off the coast of Andhra Pradesh.The capacity of the Refinery was augmented in through expansion of the Refinery comprising of one Crude Distillation Unit (CDU-II) and one Delayed Coking Unit (DCU-II). A bottling plant of capacity 22000 MTPA was added to the complex and commissioned on March.

3.**The Digboi Refinery** was set up at in 1901 by Assam Oil Company Limited. The Indian Oil Corporation Ltd. took over the refinery and marketing management of Assam Oil Company Ltd. with effect from and created a separate division. This division has both refinery and marketing operations. The refinery at Digboi had an installed capacity 0.50 MMTPA (million metric tonnes per annum). The refining capacity of the refinery was increased to 0.65 MMTPA by modernization of refinery in July, A new delayed Unit of 1,70,000 TPA capacity was commissioned in. A new Solvent Dewaxing Unit for maximizing production of wax was installed and commissioned in 2003.

4.**Kochi Refineries Ltd (KRL),** is an operator of oil refinery located at Kochi India, Kerala. The company, formerly known as Cochin Refineries Ltd., was set up in pursuance of a formation agreement dated April 27,1963 was formally registered on September 6, 1963 at Ernakulam. The company was established by the Government of India.Philips Petroleum was also the prime contractors for the construction of the refinery. They entrusted the work to Pacific Procon Limited. Construction work started in March 1964 and the first unit came operational in September 1966. The installed capacity of 2.5 MMTPA was increased to 3.3 in September 1973, and to 4.5 MMTPA in 8 November 1994. The capacity of the Oil Refinery was further increased to 7.5 MMTPA in December1995.

5.**Visakh Refinery** is one of the two refineries of HPCL, the other being Mumbai Refinery. In 1957, Visakh Refinery went on stream under the ownership of M/s Caltex India Ltd. In May, 1978, M/s Caltex Oil Refinery (India) was amalgamated with Hindustan Petroleum Corporation Ltd. The installed capacity of 1.5 MMTPA was increased to 4.5 MMTPA in 1985 and 7.5 MMTPA in 1999, through an expansion programme.

PRODUCTION STATISTICS: The free world's consumption of petroleum in 1982 was 2.69 X I09 m 3 , down from the 1979 peak of 3.04 X 109 m 3 . Total world consumption was estimated at 5.59 X 109 m3 / year. U.S. oil fields produce approximately 14 percent of the world's petroleum as shown in Table. Most of the free-world fields, except those of OPEC (Organisation of Petroleum Exporting Countries), are currently producing at maximum rates. No industry publishes more extensive statistical data than does the petroleum industry through the API (American Petroleum Institute) and other data-collecting agencies.

4. Research and development

Petroleum, the product of natural changes in organic materials over millennia, has accumulated beneath the earth's surface in almost unbelievable quantities and has been discovered by humans and used to meet our varied fuel wants. Because it is a mixture of thousands of organic substances, it has proved adaptable to our changing needs.

PRODUCT EVALUATION:

Major parameters for gasoline and diesel specification are given below

Major Parameters of Gasoline Specifications

Major parameters for gasoline included in Bharat or Euro norms are

• Lead phase out

• Lower RVP

• Lower benzene & aromatics

• Lower olefin content

• Limited Oxygen content

• Lower Sulfur content

Other parameters of importance are RON, MON, Lead, gum, oxidation stability, density, VLI index, FBP. In case of reformulated gasoline aromatics, olefins oxygen, Antiknock index, vapor lock index

Major Parameters of Diesel Specifications

Major parameters for diesel included in Bharat or Euro norms are

• Low sulfur • Low aromatics

• High cetane number

• Lower density

• Lower distillation end point

Other parameters for diesel are density, viscosity, cetane number distillation range, sulphur, carbon residues, oxidation stability, Flash point, acid value, ash and water contents.

EVALUATION OF FEED STOCKS FOR PETROCHEMICALS (OLEFIN, AROMATICS, AND LINEAR ALKYL BENZENE (LAB) PLANTS)

Olefin , aromatic and LAB production are three major Petrochemical building blocks. Various feed stocks olefins, aromatics and surfactants are given.

Input cost of feed constituents is a major portion of the variable cost of production in petrochemical plants. Major feed input olefin, aromatics and surfactants are Ethane propane from natural gas, naphtha, kerosene from the refinery and LPG from refinery, pyrolysis gasoline from steam crackers, Benzene from aromatic plant. Feed quality monitoring and improvement efforts are therefore very important aspects having significant impact on the economics of the operation cost. The precursors and undesirable constituents in feed including catalyst and adsorbents poisons should be known, analyzed and monitored continuously.

Plant	Feed stock
OLEFINS	Ethane, Propane, Naphtha, Gas oil
AROMATICS	Naphtha, Pyrolysis gasoline, LPG
LAB	Kerosene for paraffins, benzene

Table: Feed stocks for Olefin, Aromatics ans LAB

OLEFIN PLANTS

Olefins playing important role in petrochemical industry by providing raw materials for chemical intermediates like ethylene oxide ethylene glycol, acetaldehyde, vinyl chloride etc and poly olefins. Olefin production requires more paraffinic naphtha.

Desired components in feed for olefins productions:

Naphthenes: Naphthene yield olefins of higher carbon number. Butane yield increases appreciable with naphthenic feed. Naphthenes also enhance production of aromatics.

Aromatics: The aromatics is feed are highly refractory and they pass through the furnace unreacted.

Sulphur: The sulphur in feed suppress stream reforming reaction catalyzed by nickel present in radiant coil. Optimum level of sulphur is 1 ppm.

Physical Properties: Density, distillation range are useful and give a rough assessment of feed quality.

Ethylene: The following components in feed give ethylene in decreasing order:

- Ethane, Butane to Decane, 3 and 2 Methyl hexane, 2 methyl Pentane/ 2,2 Dimethyl Butane, Isopentane

Propylene: The following components in feed give propylene in decreasing order:

- Isobutane, n-nutane, n-propane, 3 methyl pentane, 2,3 dimethyl butane, 2 methyl hexane, n-pentane, 3 methyl hexane, iso pentane.

Butadiene: The following components of feed give butadiene is decreasing order:

- Cyclo hexane, methyl cyclo pentane.

Some of the key properties for evaluation of naphtha for olefin production are density, ASTM distillation, TBP, FBP, Saybolt colour, sulphur, RVP and paraffin, naphthanes and aromatics content

.

5. Summary

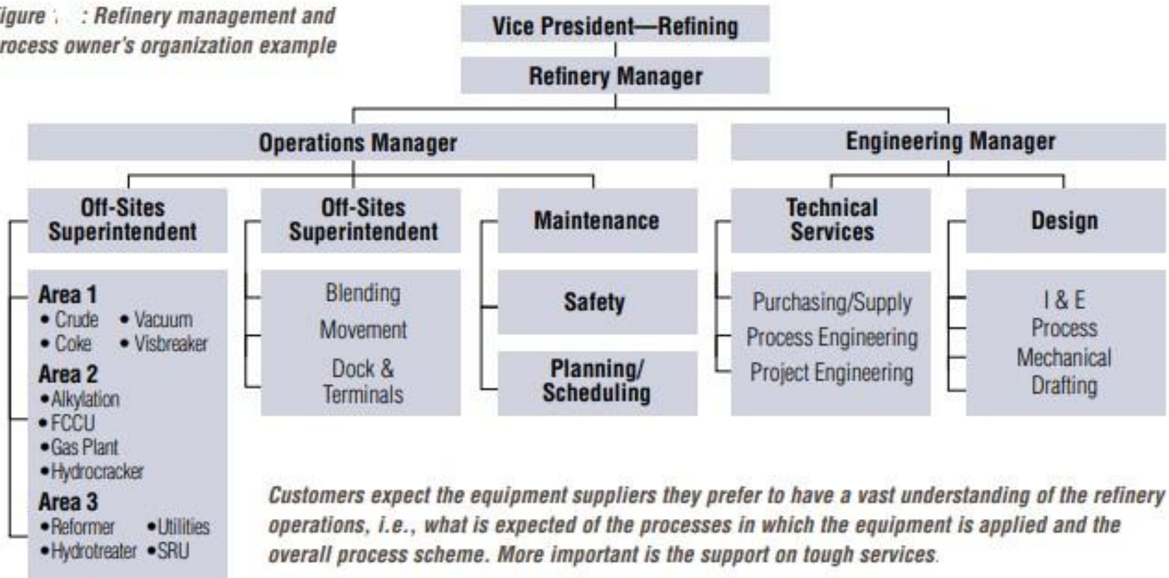
- Petroleum Refinery Engineering is one of the most important areas of Chemical Enginering. It serves the purpose of fuel production along with a great variety of hydrocarbons. Refineries are one of the largest plants and supply all the major day-to-day working substances. The Diesel and Petrol/Gasoline have significant impacts on the economy as well as the environment. Refining comes after the oil exploration process and drilling and the crude obtained through these processes is finally transported to the refinery. The refinery then removes the salts and water content present in the oil and pre-heats it.

- Next, the crude oil is sent to the Crude Distillation Unit , also called the Atmospheric Distillation Unit, where the crude is distilled at various cuts as per the boiling points of various components of the crude oil. The lighest components like light hydrocarbons such as C1-C2 , then C3-C4 are recovered at the top whereas the heaviest components i.e. mainly the gas oil,residue,etc. , is sent to the Vacuum Distillation Unit , which operates under vacuum in order to decrease the boiling poin t of the feed and hence, attain distillation at a much lower temperature.

- The main CDU products as per their increasing weight along with increasing temperature are light gases, LPG,Naphtha, Gasoline ,Kerosene/Jet fuel, Diesel, Gas Oil. However, these products are further treated and processed as they contain a lot of contaminants and are still not suitable for use. The hydrotreater, gas treating, mercaptan removal,etc. are various treating methods in order to get the desired products from the refinery.

- The vacuum distillation unit (VDU) operates under vacuum and produces the heavy gas oils, resid and heavier products like coke, asphalts,etc. The resid conversion is one of the important preocesses and the top product of the VDU is hydrotreated and sent to the hydrocracker to produce more of Diesel and fuiel oils.

Figure : Refinery management and process owner's organization example



1. Appendix: All the assignment-

Assignment – 1

***Ques*- Kindly explain the major elements in details which we consider to establish a new refinery in a particular area of a country including safety aspects.**

***Answer*-**

Factors responsible for location of Industries:-

Industrial locations are complex in nature. These are influenced by the availability of many factors. Some of them are: raw material, land, water, labor, capital, power, transport, and market.

For ease of convenience, we can classify the location factors into two: geographical factors and non-geographical factors

Geographical Factors:-

Raw material: Availability of natural resource that can be used as raw material.

Technology: To turn the resource into an asset with value.

Power: To utilize the technology.

Labour: Human resource in the area who can function as labor to run the processes.

Transport : Road/rail connectivity.

Storage and warehousing.

Marketing feasibility.

Characteristics of land and soil.

Climate.

Precipitation and water resources.

Vulnerability to natural resources

Non-geographical Factors:- Capital

investment.

Availability of loans.

Investment climate.

Government policies/regulations.

Influence of pressure groups.

Refineries and plants have specialized fire safety needs. API strongly supports the principles of fire prevention as elements for personnel and property protection in the petroleum industry. Prevention programs provide the most effective means of ensuring personnel safety. API provides a forum for its members to share information and develop industry standards to advance safety and loss prevention programs. Currently, API maintains about 30 safety and fire protection standards and recommended practices.

API members are committed to protecting the health and safety of their workers and the community. To this end, the refining industry has made significant investments in programs, training, standards and practices, and equipment that have led to occupational and process safety performance improvements. These investments continue as part of the industry's overall continuous improvement effort.

API has developed and maintains more than 180 refining safety and operational standards and recommended practices under its American National Standards Institute (ANSI) accredited program. API and its member companies are committed to ensuring that all industry standards contain the latest science and technologies, they recognize proven industry practices and incorporate lessonslearned from past incidents and near misses. These standards have been incorporated by reference into Federal, State and International regulations.

API member companies are committed to conducting business in a manner that protects the safety and health of their employees, others involved in their operations, customers, and the public. Process safety is part of safety management and focuses on the concerns of major hazards impacting, safety, environmental damage and business losses. The goal of process safety management is to develop plant systems and procedures to prevent unwanted releases that may ignite and cause toxic impacts, local fires or explosions.

Assignment – 2

Ques- Explain in details , What is importances of FCC & Hydro cracker units in a refinery in BS-VI scenario and why AVUs known as mother unit of any refinery ?

Answer:-

Fluid catalytic cracking (FCC), a type of secondary unit operation, is primarily used in producing additional gasoline in the refining process.

Cracking, in petroleum refining, the process by which heavy hydrocarbon molecules are broken up into lighter molecules by means of heat and usually pressure and sometimes catalysts. Cracking is the most important process for the commercial production of gasoline and diesel fuel.

BS-VI auto fuel emission standards mandate all Indian refiners to produce diesel with <10 ppmw sulphur content from January 2020 onwards. There are numerous challenges in the design and operation of an ultra-low sulphur diesel (ULSD) producing hydrotreater. Experience is that most of the challenges in a ULSD producer’s operation can be addressed by establishing the appropriate process basis at the design stage.

Cracked gasoil from delayed cokers, FCC units or visbreakers will have two or more times the sulphur, nitrogen, metals and aromatics content of straight run diesel. Therefore the right strategy will be to design the catalyst and hydrogen (make-up and recycle compressors) circuit for a good amount of cracked gasoil feed. The heat integration and feed effluent exchanger design should consider the correct volume of lean olefin and/or cold feed as the design basis for robust operation. Such a feed case, along with key process design aspects which will ensure robust design and operation in a diesel hydrotreater, are discussed in this article. Fail-safe options/strategies for refiners in the event of critical equipment failures, such as in combined feed exchangers, which may call for shutdown or slow-down to enable sustainable production of BS-VI diesel, are described.

The article also highlights the challenges in logistics for storage, transfer and despatch of BS-VI diesel along with the means to address these challenges.

ADU is a unit which is the first unit in crude oil processing and before entering this unit the crude oil is heated to a elevate temperature in a preheat train.This column operates at atmospheric pressure and different cuts(Light cycle oil,heavy cycle oil etc…) of crude oil are separated from different plates of the distillation column.The bottom residue of this column is send to vacuum distillation unit for further processing. That's why it is known as mother unit.

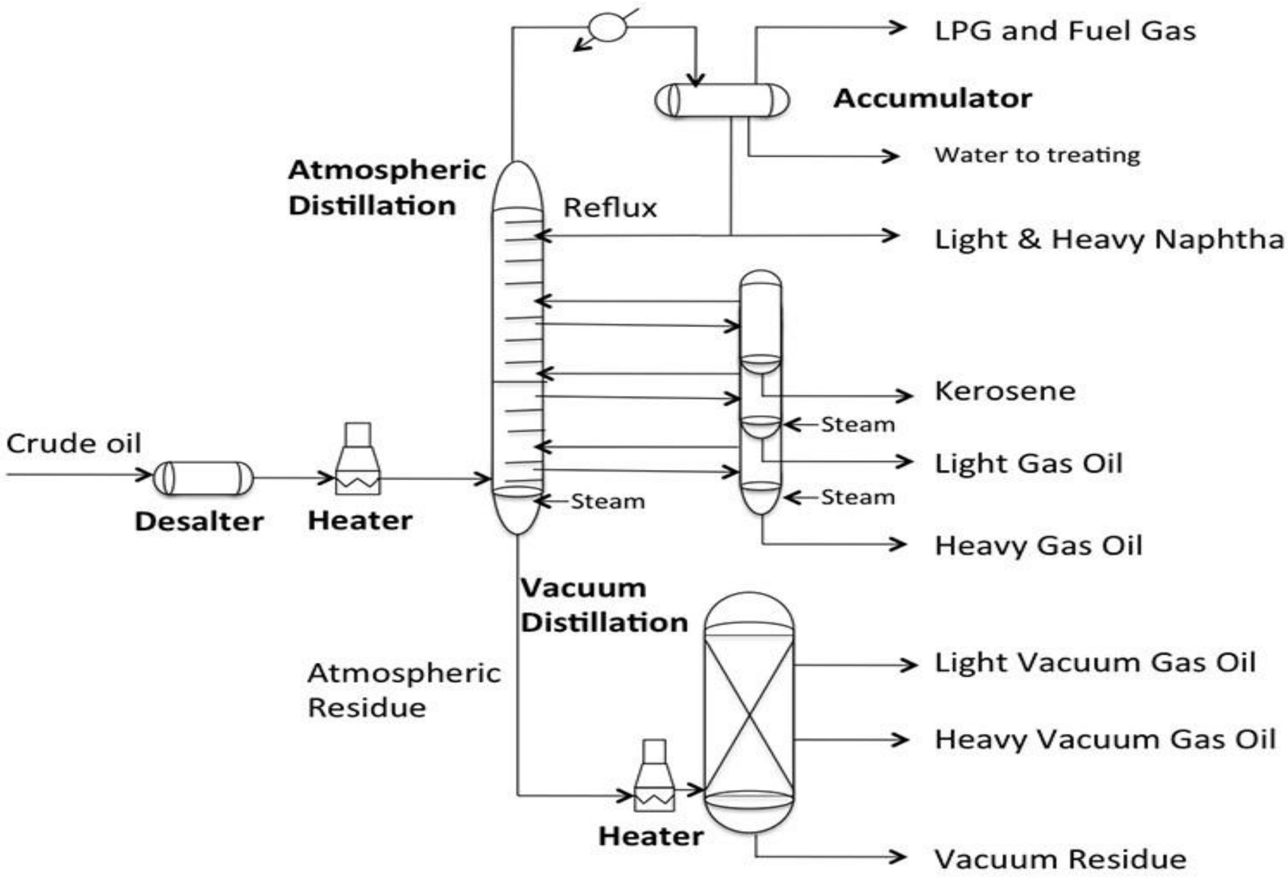


Fig. Atmosphere and Vacuum Distillation

Assignment – 3

Ques- **Explain in details , what are critical operation controls of HGU, DCU, ISOM, DHDS & DHDT. What are the monitoring system of HGU & DHDT catalyst performance ?**

***Answer*:-**

Full Form of Units:-

1. HGU- Hydrogen Generation Unit
2. DCU- Delayed Coking Unit
3. ISOM- Isomerization Unit
4. DHDS- Diesel Hydro-Desulphurization Unit
5. DHDT- Diesel Hydro-Treatment Unit

Hydrogen Generation Unit (HGU)

Objective : To Meet the Hydrogen requirement for DHDS/DHDT/OHCU/ISOM/Reforming Units and Other Hydrotreaters.

Feed : Natural Gas / Naphtha and Feed

Catalyst :
Co-Mo for Hydrotreater
ZnO/K2Co3 for H2S and Chloride adsorber
NiO for Preformer
Ni for Reformer
CuO for HT/LT Shift reactors
Adsorbents(molecular sieves) for PSA Adsorbers

HGU Product is 99.99% Pure H_2

Operating Conditions :

- Temperature range : 860-870 °C
- System Pressure : 20-38 kg/cm^2

Even traces of sulphur is poison to Reformer Catalyst. Sulphur guard is provided to reduce feed sulphurto <50 ppb. Pre Reformer reduce the load on the reformer by converting the heavier molecules to methane at relatively lower temperature.

The Shift reactor maximize the H2 production by Shift reaction (i.e. CO $+H_2O \rightarrow H_2 + CO_2$).

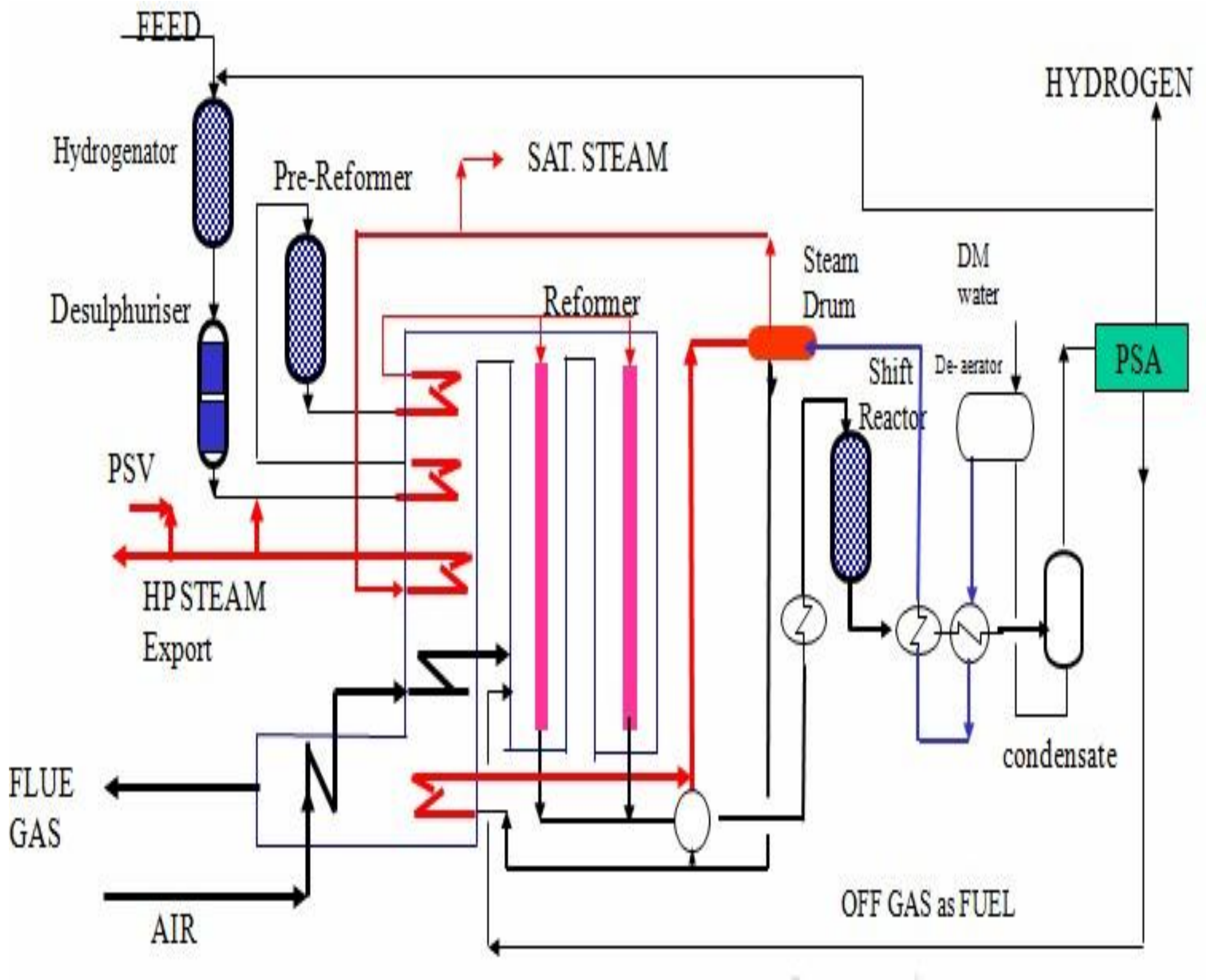


Fig. Hydrogen Generation Unit

In IOCL mathura refinery there are two hydrogen generation units:

HGU-I & HGU-II

HGU-I:

The Hydrogen plant is designed for production of 34,000 MTPY of Hydrogen. Process licensor for HGU is HTAS, Denmark. The plant is divided into 3 sections.

- Desulphurization
- Reforming
- CO-Conversion

FEED

The hydrogen generation unit can be fed either by naphtha or natural gas. The naphtha feed is pressurized to about 35 Kg/cm2g by one of the naphtha feed pumps and sent to the desulphurization section.
The pressurized feed is mixed with recycle hydrogen from the hydrogen header. The liquid naphtha is evapourated to one of the naphtha feed vapourizers. The hydrocarbon feed is heated to 380°-400 ^{O}C by heat exchange with superheated steam in the naphtha feed pre-heater.

HGU-II:

The Hydrogen plant is designed for production of 74,000 MTPA of Hydrogen. Here also stem reforming of natural gas or naphtha is done to produce hydrogen.

HGU-II has following processes:

- Feed predesulfurization
- Feed desulfurization

- Pre-reforming
- Reforming
- High Temperature shift Reaction
- Low Temperature shift reaction

HGU-II Furnace has top fired burners. HGU-II has 12 PSA Drums.

Delayed Coking Unit (DCU)

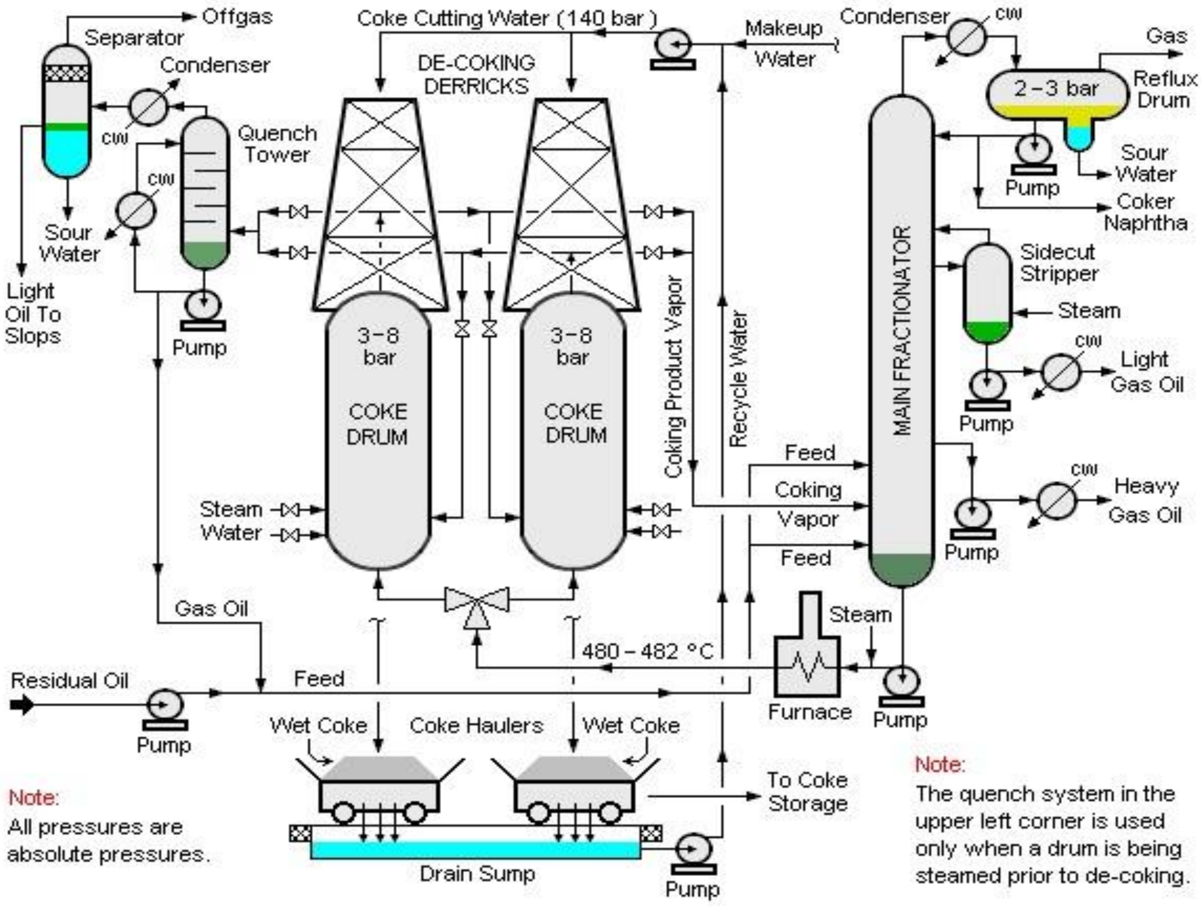


Fig. Delayed Coking Unit at Low Pressure

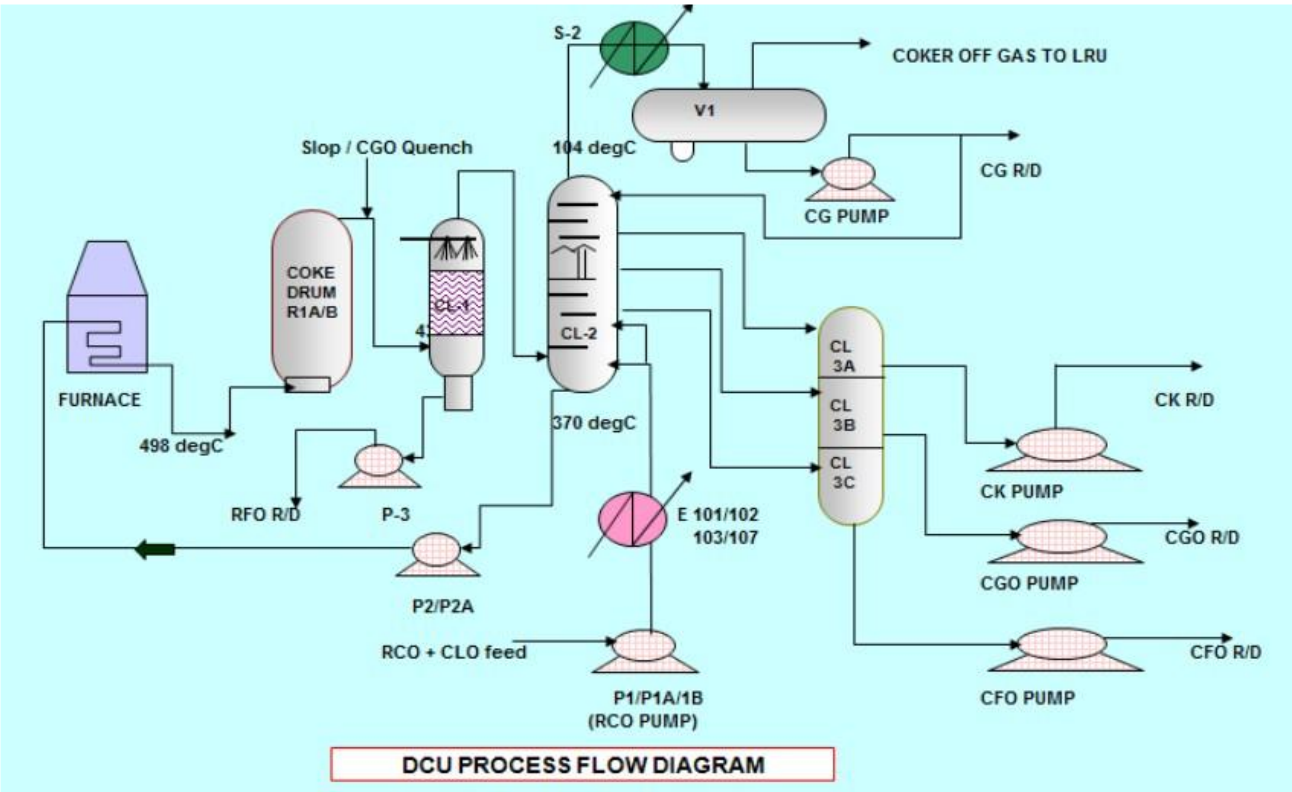


Fig. DCU at High Pressure

FEED STOCK SELECTION:-

- Amount of coke formed related to the carbon residue of the feed
  - » Since this parameter correlates well with hydrogen/carbon atomic ratios and indicates coking tendencies, this parameter is especially useful for screening feeds
  - » Three main tests
    - ✧Ramsbottom method (ASTM D-524)
    - ✧Conradson Carbon (ASTM D-189)
    - ✧Microcarbon Residue Test

Methods of minimizing Pet Coke production:-

1. **Coke yield in DCU are variables of following parameters:**
   - **Feed CCR-** higher CCR increases coke yield – but better from point of view of value addition- **thus should not be targeted**
   - **Recycle ratio (RR)-** higher recycle ratio increases coke yield- **should be targeted**
   - **Reactor pressure-** higher pressure increases coke yield- **should be targeted but will be restricted to WGC suction pressure & system pressure drop**
   - **COT-** Higher COT reduces coke make but increases gas make, reduces run length and coke cutting takes more time (hard coke) - **to be optimised**
   - **Space velocity-** higher the space velocity lower the coke make- **to be targeted in a limited way as it may result into coke carry over from reactor to MF column.**

2. **Formula to predict coke make in DCU**
   - **As per Solomon:** 1.35 * CCR (does not take care of RR)
   - **Thumb Rule:** CCR * 1.4 + RR * 11% (better for day-to-day monitoring)
   - **More scientific formula: (Ref Paper on Fundamentals of Delayed Coking Joint Industry Project, University of Tulsa)**

Coke make = 0.9407*CCR-0.0609*T+0.1529*P-319.759* LSV+ 65.075

with R^2 value of 0.97

T- temp in ^{0}F, **P- Pressure in PSIg,** **LSV- Liq Space velocity**

Effect on operating Variables:-

- Pressure and Temperature
  - » Trend to lower pressures
    - ✧ Coke drums normally 25 psig but 15 psig common
    - ✧ Pressure dictated by the suction pressure of gas compressor removing vapors from fractionator overhead accumulator drum
  - » Lower pressures & higher temperatures increase gas oil yields by favoring cracking reactions
    - ✧ Increase the load on the gas compressor
    - ✧ Increase probability of shot coke formation, foaming, & coke carryover
- Recycle Ratio
  - » Low recycle ratios common — increase gas oil yields & decrease coke yields
    - ✧ Contaminants produced with the gas oil, lowering quality
    - ✧ Contaminates increase probability of shot coke formation, foaming, & coke carryover

Improvement through operational measures minor hardware change:-

- Maximising t'put & on stream factor
- Reduction in Recycle Ratio & Coke drum pressure
- Reduction in Chamber Cycle time
- Regular online spalling of Heaters- to increase heater run length
- Propylene recovery from off gas
- Improved spray nozzle & trays in HCGO wash zone
- Filtration system for hot HCGO before processing in Hydrocracker.
- Stripping of CFO (in high pressure cokers) to recover gas oil/ modifying CFO zone trays.
- Heat integration/ maximising hot feed supply
- Improved coke cutting/ handling/ conveying systems
- Improved Heater metallurgy
- Coker additives for reduction in coke yield & increase of liquid yield

ISOMERIZATION UNIT

Introduction - The basic principle of Isomerization is to straight chain alkanes to side chain paraffins. This enhances the octane number substantially - For instance, npentane has an octane number of 61.7 where asiso-pentane has an octane number of 92.3 - Usually light naphtha is used as a feed stock

Process parameters –

Reactor pressure: 4 – 24 barg

Reactor temperature: 500 – 525 oC

H2/Hydrocarbon molar ratio: 2 – 3

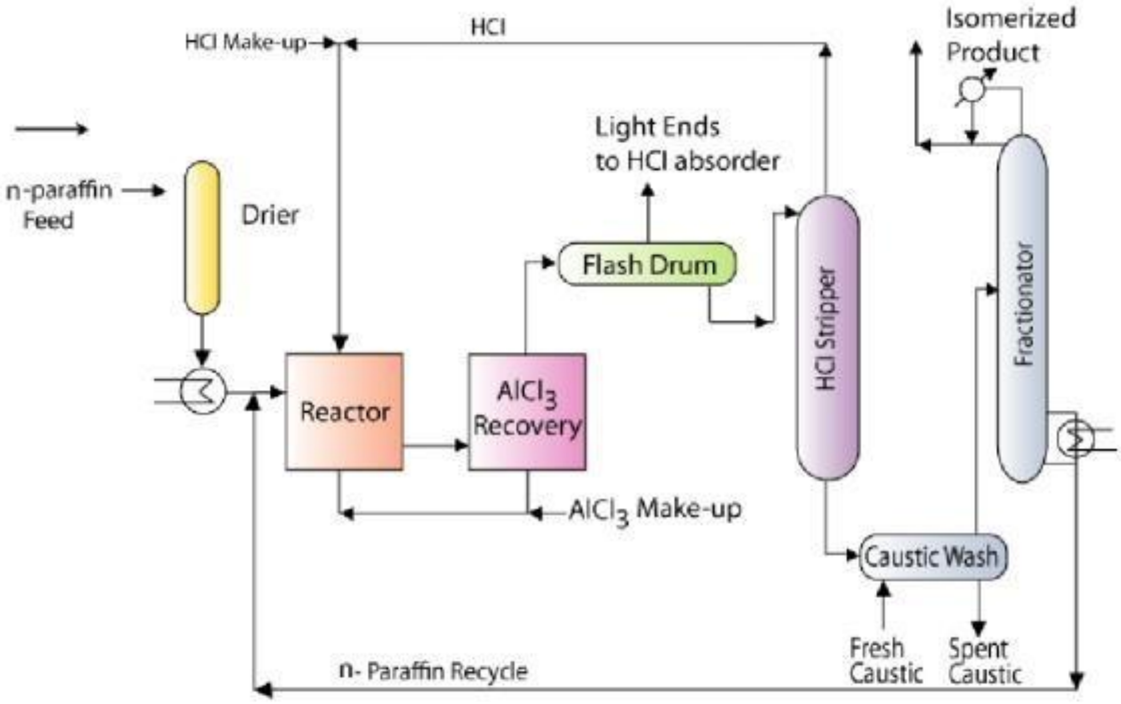
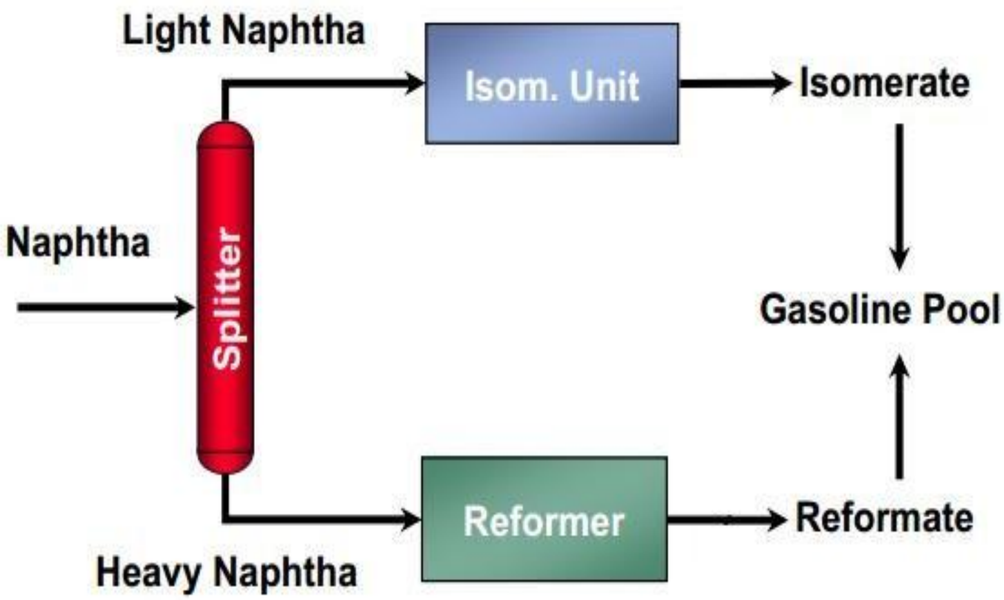


Fig. Flow sheet of Isomerization of n-paraffin

- **Generate high quality gasoline blend stock**
- **Saturate benzene**
- **Consume benzene precursors**



Catalyst –

Platinum base catalysts are used

$AlCl_3$ is used as a promoter for the catalyst

During reaction, part of the $AlCl_3$ gets converted to HCl

Therefore, completely dry conditions shall be maintained to avoid catalyst deactivation and corrosion

Catalytic reaction takes place in the presence of hydrogen to suppress coke formation

Diesel Hydro Desulfurization Unit (DHDS)

DHDS (Diesel hydro desulphurization unit) is set up for the following purposes:

- A step towards pollution control
- To produce low sulphur diesel (0.25 w/w %) as per govt. directive w.e.f. Oct. 1999.

Feed consists of different proportion of straight run LGO, HGO, LVGO and TCO. Mainly two proportions are used:

- 74% SR LGO, 21% SR HGO, 5% SR LVGO
- 48% SR LGO, 24% SR HGO, 8% SR LVGO, 20% TCO

The DHDS unit treats different gas oils from various origins, straight run or cracked products. The feed is a mixture of products containing unsaturated components (diolefins, olefins), Aromatics, Sulfur compounds and Nitrogen compounds. Sulfur and nitrogen contents are dependent upon the crude.

The purpose of DHDS Unit is to hydro-treat a blend of straight run gas oil and cracked gas oil (TCO) for production of HSD of sulfur content less than 500 ppm wt.

The Hydrodesulphurization reaction releases H_2S in gaseous hydrocarbon effluents. This H_2S removal is achieved by means of a continuous absorption process using a 25% wt. DEA solution.

In addition to the desulphurization, the diolefins and olefins will be saturated and a denitrification will occur. Denitrification improves the product stability. The hydrogen is supplied from the hydrogen unit. Lean amine for absorption operation is available from Amine Regeneration Unit (ARU). Rich Amine containing absorbed H_2S is sent to ARU for amine regeneration.

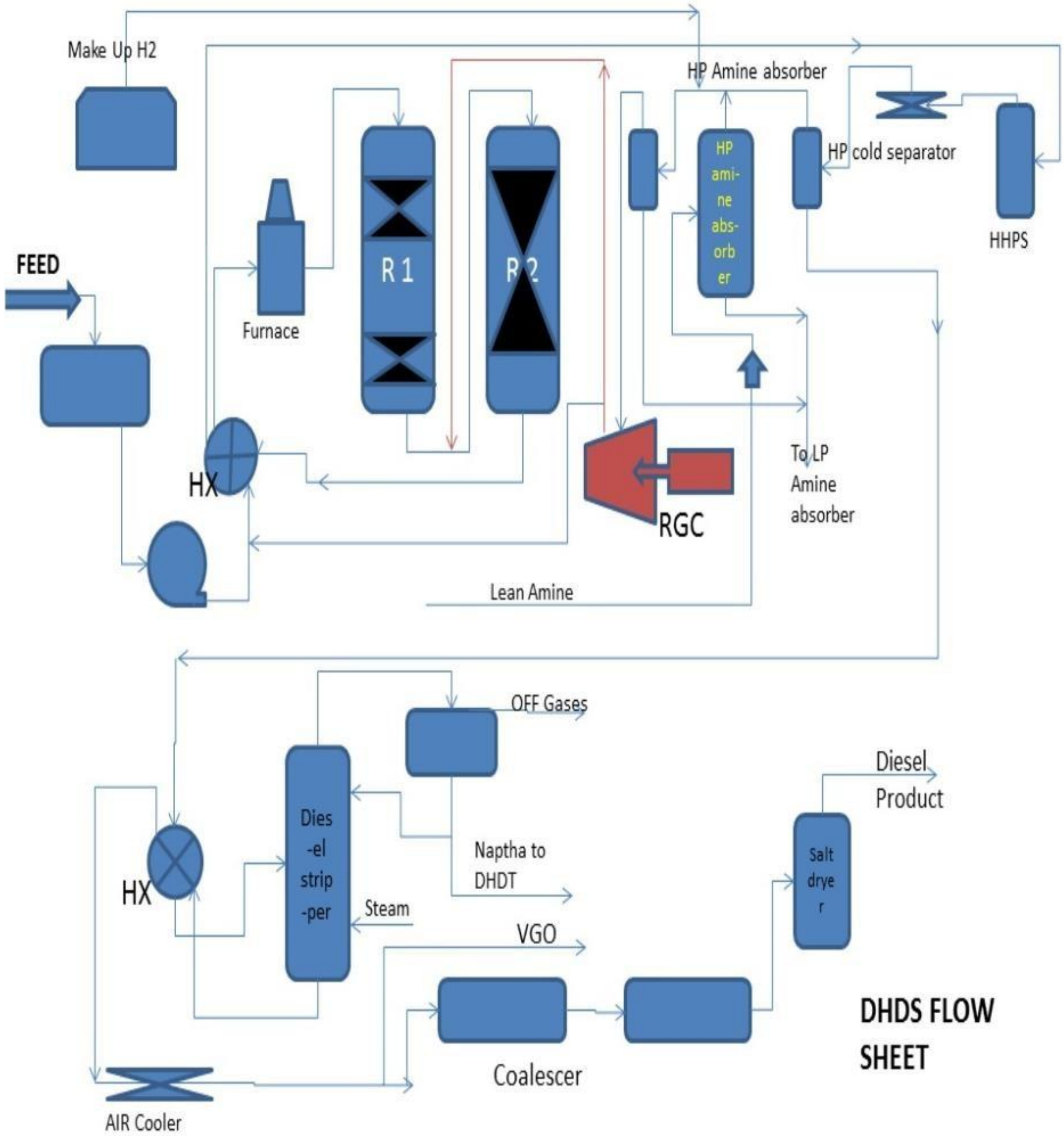
CATALYSTS

Catalysts used for this process are HR-945 and HR-348/448.The HR-945 is a mixture of nickel and molybdenum oxides on a special support. Nickel has been selected because it boosts the hydrogenating activity. The HR-348 and HR-448 are desulphurization catalysts; it consists of cobalt and molybdenum oxides dispersed on an active alumna. Its fine granulometry and large surface area allow a deep desulphurization rate.

Different catalysts based on Nickel and Molybdenum Oxide are used to enhance the rate of reactions.

Products Yields:

Sl. No.	Products	wt%
1	Off-Gas	1.36
2	Wild-naptha	1.04
3	Diesel	97.1



DHDS FLOW SHEET

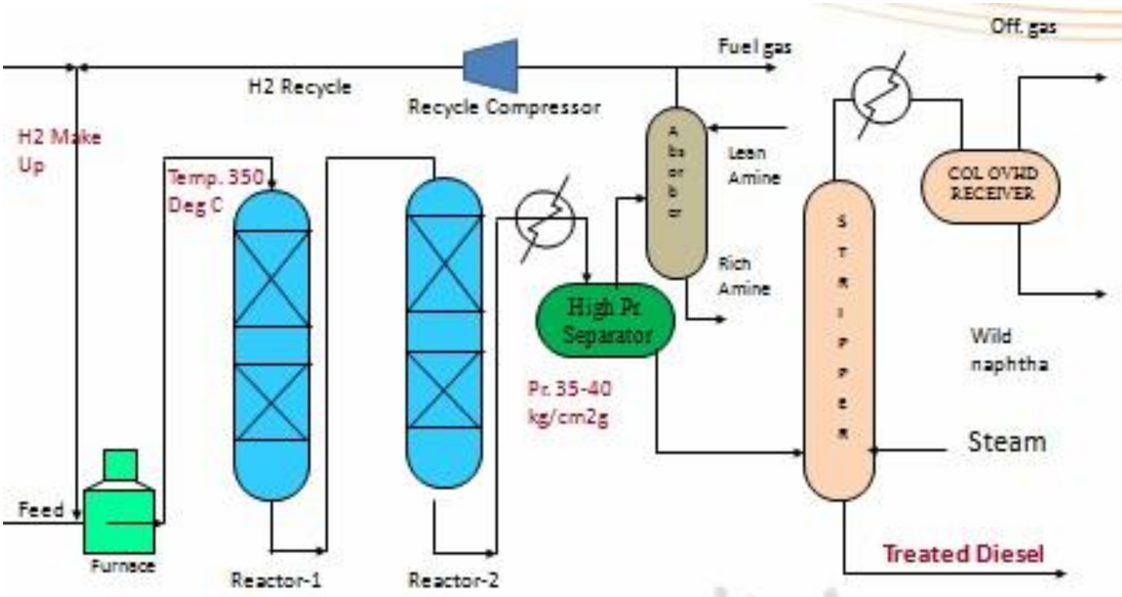


Fig. DHDS

DHDS Product Yields & Operating Conditions

1. Typical Product Yields

Sl.no.	Products	Wt%	End Users
1.	Off Gas	1.36	Refinery Fuel gas system after Amine Wash
2.	Wild Naphtha	1.34	To Naphtha Pool after stabilisation
3.	Diesel	98.0	To Euro II Diesel Pool

2. Operating Conditions :

Temperature range : 320 -380 DEG C

System Pressure : 35 -40 kg/cm2(g)

Diesel Hydro Treatment Unit (DHDT)

Objective : To meet the EURO-III/IV diesel quality requirement (<350/50 ppmS)

Feed : Straight run diesel / FCC diesel component/ Coker and Visbreaker diesel components.

Catalyst : Ni-Mo oxides

Products Yields:

Sl. No.	Products	wt%
1	Off-Gas	2.65
2	wild-naphtha	2.8
3	Diesel	96.1

Wild naphtha feed from existing DHDS unit is processed along with DHDT wild naphtha in a stabilizer located inside DHDT battery limits for producing single naphtha product.

Processes in DHDT:

- **Refining & hydrogenation:**

Removal of heteroatom (S, N_2, O_2) Saturation of olefins and dioelfins.

- **Hydrodesulfurization:**

Hydrodesulfurization reactions are fast and take place in single step.

Mercaptans: $\mathbf{R\text{-}SH + H_2} \quad \mathbf{R\text{-}H + H_2S}$

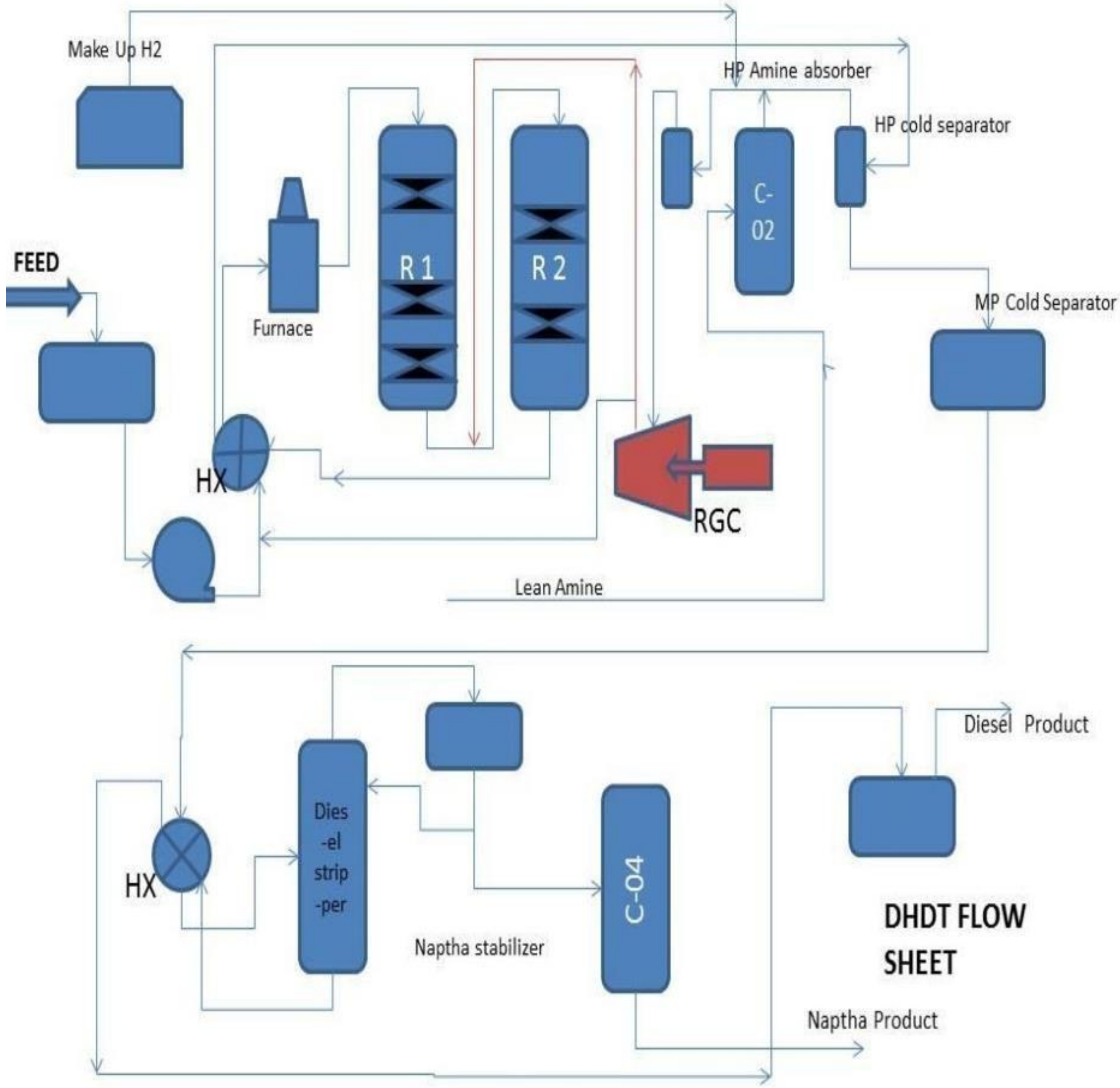
Sulfides: $\mathbf{R\text{-}S\text{-}R + 2H_2} \quad \mathbf{2R\text{-}H + H_2S}$

- **Hydrogenation:**

Aromatic saturation & denitrification of heterocyclic compounds.

- **Hydrocracking:**

Hydroisomerisation & then cracking into lighter isoparaffins.


Make Up H2
HP Amine absorber
HP cold separator
FEED
Furnace
R 1
R 2
C-
02
MP Cold Separator
HX
RGC
Lean Amine
Diesel Product
Dies
-el
strip
-per
C-04
HX
Naptha stabilizer
DHDT FLOW
SHEET
Naptha Product

DHDS & DHDT Product Yields & Operating Conditions

DHDS

Products	Wt%
Off Gas	1.36
Wild Naphtha	1.34
Diesel	98.0

Operating Conditions

Temperature range : 320-380 DEG C

System Pressure : 40 kg/cm2(g)

DHDT

Products	Wt%
Off Gas	2.5
Wild Naphtha	2.8
Diesel	96.0

Operating Conditions

Temperature range : 320-380 DEG C

System Pressure : 115 kg/cm2(g)

Catalyst Monitoring system in Refining:-

With the progress of cycle, catalyst deactivates approaching EOR conditions.The product may not meet the specifications, the reactor ΔP may be high affecting the recycle gas flow rate.

The catalyst activity may be recovered by in situ or ex situ regeneration. The coke on the catalyst is burnt under controlled conditions of temperature and air- nitrogen flow. Oxygen concentration in the reactor I/L nitrogen is monitored & air supply is strictly regulated to control reactor ΔT. Caustic scrubbing downstream of air cooler and NH3 injection in effluent exchanger is carried out to protect against sulfur oxides.

Catalyst :

Co-Mo for Hydrotreater

ZnO/K2Co3 for H2S and Chloride adsorber

NiO for Preformer

Ni for Reformer

CuO for HT/LT Shift reactors

Adsorbents(molecular sieves) for PSA Adsorbers

HGU Product is 99.99% Pure H_2

Operating Conditions :

- Temperature range : 860-870 °C
- System Pressure : 20-38 kg/cm^2

Even traces of sulphur is poison to Reformer Catalyst. Sulphur guard is provided to reduce feed sulphurto <50 ppb. Pre Reformer reduce the load on the reformer by converting the heavier molecules to methane at relatively lower temperature.

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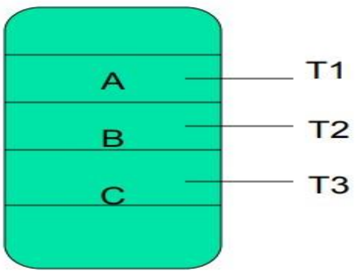
Sulfides: **$R\text{-}S\text{-}R + 2H_2$ $2R\text{-}H + H_2S$**

1.Weighted Average Bed Temp. (WABT):-

- Attribute a weight fraction of the Catalyst bed to each TI



A=25% catalyst

B=35% catalyst

C=40% catalyst eight

WABT = 0.25*T1+0.35*T2+0.4*T3

2. H2 to Oil Ratio:-

- It affects bed Δt
- Improves distribution of materials
- Reduces over-cracking
- Suppresses coke formation

3. Pressure:-

- Hydrogen Pressure is key
- Required Pressure is determined by:
  - Feedstock
  - Desired product quality
  - Desired Cycle life
- Higher pressure or higher purity
- Inhibits coke formation

H_2 Partial Pressure = Recycle Gas H_2 purity * Pressure

The End!!!!