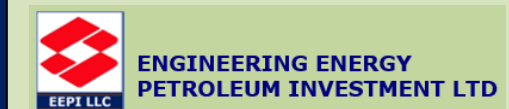
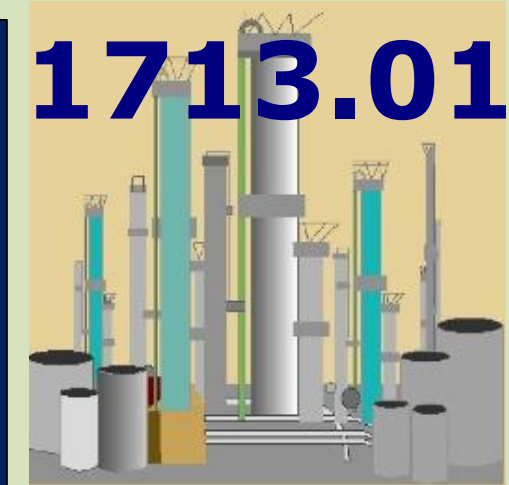




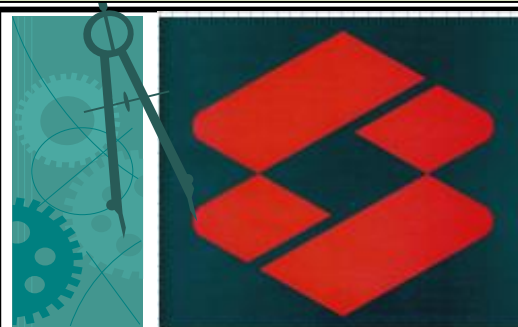
WHITE DOLPHIN REFINERY BASIC PROCESS AND BLOCK DIAGRAMS



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Petroleum Refining Overview

In this study, we present a brief overview of the petroleum refining, a prominent process technology in process engineering.

3.1 Crude oil

Crude oil is a multicomponent mixture consisting of more than 108 compounds. Petroleum refining refers to the separation as well as reactive processes to yield various valuable products. Therefore, a key issue in the petroleum refining is to deal with multicomponent feed streams and multicomponent product streams. Usually, in chemical plants, we encounter streams not possessing more than 10 components, which is not the case in petroleum refining. Therefore, characterization of both crude, intermediate product and final product streams is very important to understand the processing operations effectively.

3.2 Overview of Refinery processes

Primary crude oil cuts in a typical refinery include gases, light/heavy naphtha, kerosene, light gas oil, heavy gas oil and residue. From these intermediate refinery product streams several final product streams such as fuel gas, liquefied petroleum gas (LPG), gasoline, jet fuel, kerosene, auto diesel, lubricants, bunker oil, asphalt and coke are obtained. The entire refinery technology involves careful manipulation of various feed properties using both chemical and physical changes.

Conceptually, a process refinery can be viewed upon as a combination of both physical and chemical processes or unit operations and unit processes respectively. Typically, the dominant physical process in a refinery is the distillation process that enables the removal of lighter components from the heavier components. Other chemical processes such as alkylation and isomerisation are equally important in the refinery engineering as these processes enable the reactive transformation of various functional groups to desired functional groups in the product streams.

3.1 Feed and Product characterization

The characterization of petroleum process streams is approached from both chemistry and physical properties perspective. The chemistry perspective indicates to characterize the crude oil in terms of the functional groups such as **olefins, paraffins, naphthenes, aromatics and resins**. The dominance of one or more of the functional groups in various petroleum processing streams is indicative of the desired product quality and characterization. For instance, the lighter fractions of the refinery consist of only olefins and paraffins. On the other hand, products such as petrol should have high octane number which is a characteristic feature of olefinic and aromatic functional groups present in the product stream.

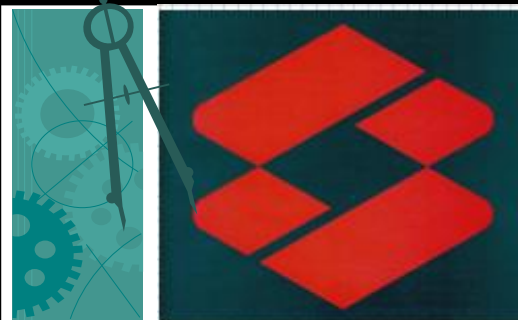
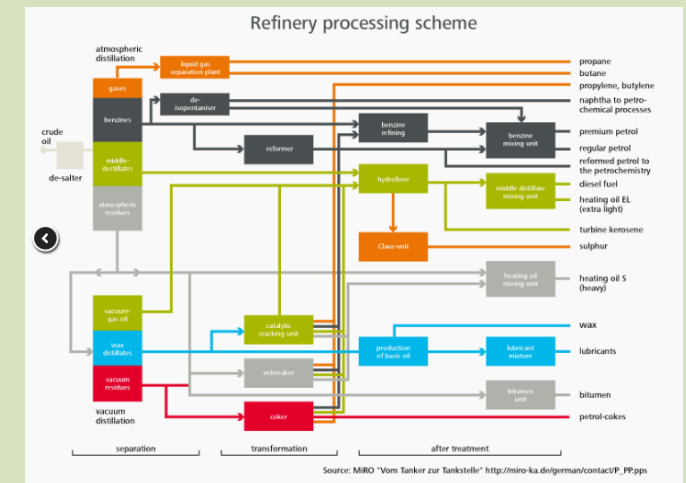
The physical characterization of the crude oil in terms of viscosity, density, boiling point curves is equally important. These properties are also indicative of the quality of the product as well as the feed. Therefore, in petroleum processing, obtaining any intermediate or a product stream with a defined characterization of several properties indicates whether it is diesel or petrol or any other product. This is the most important characteristic feature of petroleum processing sector in contrary to the chemical process sector.

The product characterization is illustrated now with an example. Aviation gasoline is characterized using ASTM distillation. The specified temperatures for vol% distilled at 1 atm. Are 158 oF maximum for 10 % volume, 221 oF maximum for 50 % volume and 275 oF maximum for 90% volume. This is indicative of the fact that any product obtained in the refinery process and meets these ASTM distillation characteristics is anticipated to represent Aviation gasoline product. However, other important properties such as viscosity, density, aniline product, sulphur density are as well measured to fit within a specified range and to conclude the produced stream is indeed aviation gasoline.

3.2 Important characterization properties

Numerous important feed and product characterization properties in refinery engineering include

- API gravity
- Watson Characterization factor
- Viscosity
- Sulfur content
- True boiling point (TBP) curve
- Pour point
- Flash and fire point
- ASTM distillation curve
- Octane number



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3.4.1 API gravity

API gravity of petroleum fractions is a measure of density of the stream.

Usually measured at 60 oF, the API gravity is expressed as $API = 141.5 / \text{specific gravity} - 131.5$ where specific gravity is measured at 60 oF.

According to the above expression, 10 oAPI gravity indicates a specific gravity of 1 (equivalent to water specific gravity). In other words, higher values of API gravity indicate lower specific gravity and therefore lighter crude oils or refinery products and vice-versa. As far as crude oil is concerned, lighter API gravity value is desired as more amount of gas fraction, naphtha and gas oils can be produced from the lighter crude oil than with the heavier crude oil. Therefore, crude oil with high values of API gravity are expensive to procure due to their quality.

3.4.2 Watson characterization factor

The Watson characterization factor is usually expressed as $K = (TB)^{1/3} / \text{specific gravity}$

Where TB is the average boiling point in degrees R taken from five temperatures corresponding to 10, 30, 50, 70 and 90 volume % vaporized.

Typically Watson characterization factor varies between 10.5 and 13 for various crude streams. A highly paraffinic crude typically possesses a K factor of 13. On the other hand, a highly naphthenic crude possesses a K factor of 10.5. Therefore, Watson characterization factor can be used to judge upon the quality of the crude oil in terms of the dominance of the paraffinic or naphthenic components.

3.4.3 Sulfur content

Since crude oil is obtained from petroleum reservoirs, sulphur is present in the crude oil. Usually, crude oil has both organic and inorganic sulphur in which the inorganic sulphur dominates the composition. Typically, crude oils with high sulphur content are termed as sour crude. On the other hand, crude oils with low sulphur content are termed as sweet crude. Typically, crude oil sulphur content consists of 0.5 – 5 wt % of sulphur. Crudes with sulphur content lower than 0.5 wt % are termed as sweet crudes. It is estimated that about 80 % of world crude oil reserves are sour.

The sulphur content in the crude oil is responsible for numerous hydrotreating operations in the refinery process. Strict and tighter legislations enforce the production of various consumer petroleum products with low quantities of sulphur (in the range of ppm). Presently, India is heading towards the generation of diesel with Euro III standards that indicates that the maximum sulphur content is about 500 ppm in the product. This indicates that large quantities of inorganic sulphur needs to be removed from the fuel. Typically, inorganic sulphur from various intermediate product streams is removed using hydrogen as hydrogen sulphide.

A typical refinery consists of good number of hydrotreaters to achieve the desired separation. The hydrotreaters in good number are required due to the fact that the processing conditions for various refinery intermediate process streams are significantly different and these streams cannot be blended together as well due to their diverse properties which were achieved using the crude distillation unit. More details with respect to the hydrotreating units will be presented in the future lectures.






3.4.3 TBP/ASTM distillation curves

The most important characterization properties of the crude/intermediate/product streams are the TBP/ASTM distillation curves. Both these distillation curves are measured at 1 atm pressure. In both these cases, the boiling points of various volume fractions are being measured. However, the basic difference between TBP curve and ASTM distillation curve is that while TBP curve is measured using batch distillation apparatus consisting of no less than 100 trays and very high reflux ratio, the ASTM distillation is measured in a single stage apparatus without any reflux. Therefore, the ASTM does not indicate a good separation of various components and indicates the operation of the laboratory setup far away from the equilibrium.

3.4.4 Viscosity

Viscosity is a measure of the flow properties of the refinery stream. Typically in the refining industry, viscosity is measured in terms of centistokes (termed as cst) or saybolt seconds or redwood seconds. Usually, the viscosity measurements are carried out at 100 oF and 210 oF. Viscosity is a very important property for the heavy products obtained from the crude

oil. The viscosity acts as an important characterization property in the blending units associated to heavy products such as bunker fuel. Typically, viscosity of these products is specified to be within a specified range and this is achieved by adjusting the viscosities of the streams entering the blending unit.

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3.4.3 Flash and fire point

Flash and fire point are important properties that are relevant to the safety and transmission of refinery products. Flash point is the temperature above which the product flashes forming a mixture capable of inducing ignition with air. Fire point is the temperature well above the flash point where the product could catch fire. These two important properties are always taken care in the day to day operation of a refinery.

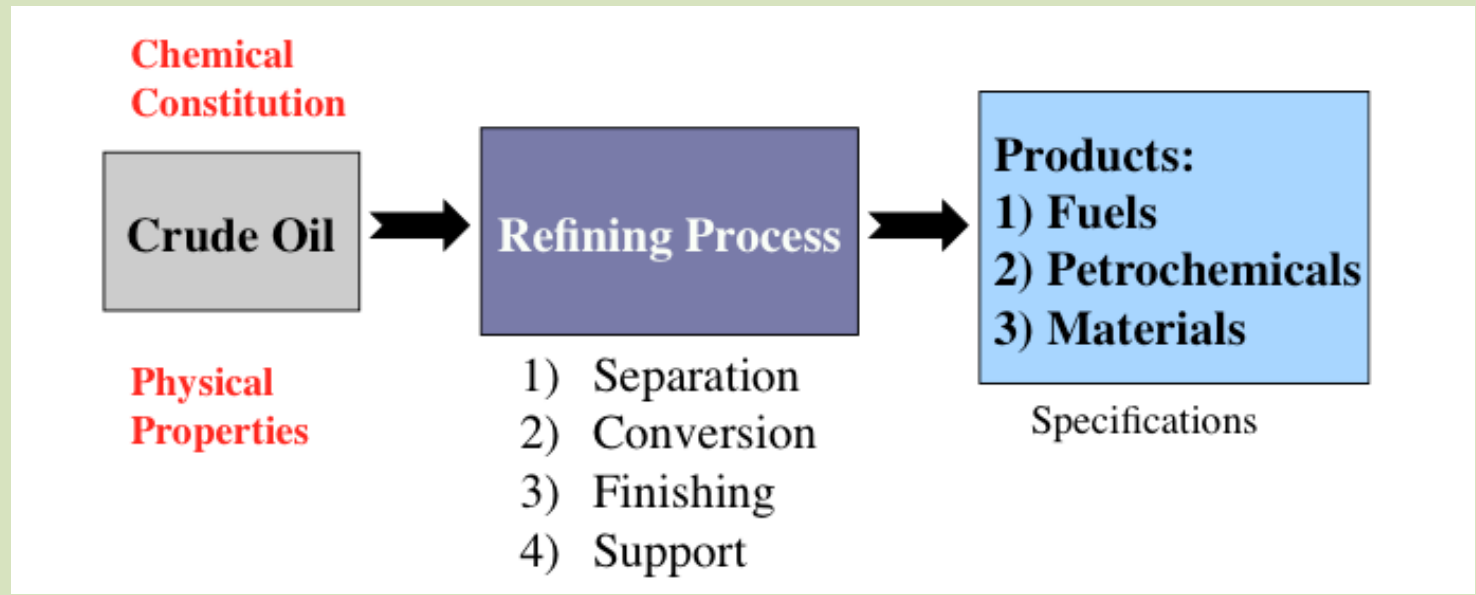
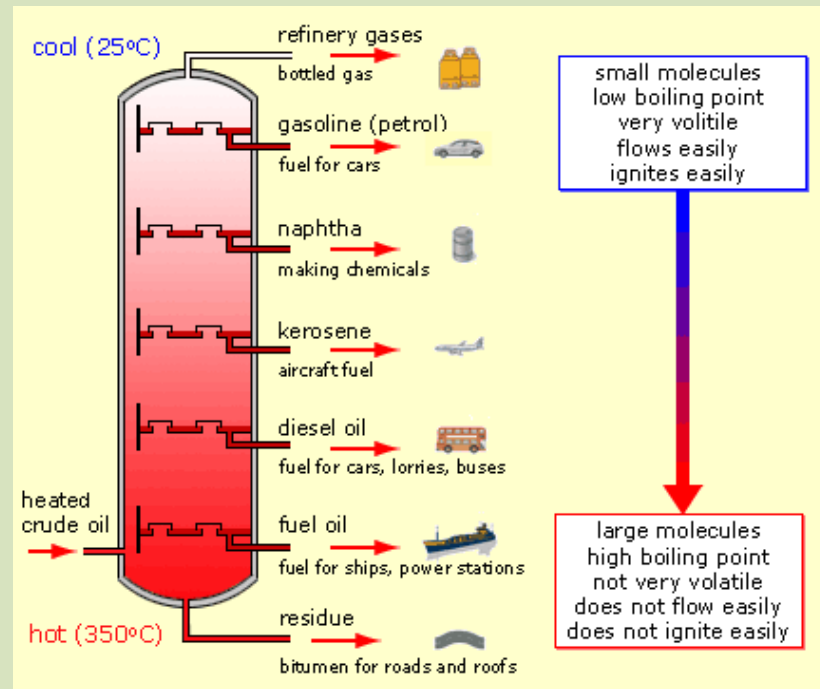
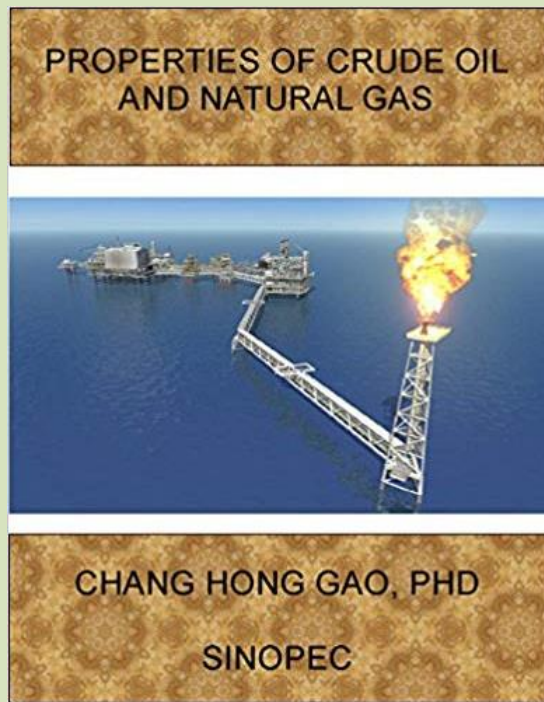
3.4.4 Pour point

When a petroleum product is cooled, first a cloudy appearance of the product occurs at a certain temperature. This temperature is termed as the cloud point. Upon further cooling, the product will cease to flow at a temperature. This temperature is termed as the pour point. Both pour and cloud points are important properties of the product streams as far as heavier products are concerned. For heavier products, they are specified in a desired range and this is achieved by blending appropriate amounts of lighter intermediate products.

3.4.5 Octane number

Though irrelevant to the crude oil stream, the octane number is an important property for many intermediate streams that undergo blending later on to produce automotive gasoline, diesel etc. Typically gasoline tends to knock the engines. The knocking tendency of the gasoline is defined in terms of the maximum compression ratio of the engine at which the knock occurs. Therefore, high quality gasoline will tend to knock at higher compression ratios and vice versa. However, for comparative purpose, still one needs to have a pure component whose compression ratio is known for knocking. Iso-octane is eventually considered as the barometer for octane number comparison. While iso-octane was given an octane number of 100, n-heptane is given a scale of 0. Therefore, the octane number of a fuel is equivalent to a mixture of a iso-octane and n-heptane that provides the same compression ratio in a fuel engine. Thus an octane number of 80 indicates that the fuel is equivalent to the performance characteristics in a fuel engine fed with 80 vol % of isooctane and 20 % of n-heptane.

Octane numbers are very relevant in the reforming, isomerisation and alkylation processes of the refining industry. These processes enable the successful reactive transformations to yield long side chain paraffins and aromatics that possess higher octane numbers than the feed constituents which do not consist of higher quantities of constituents possessing straight chain paraffins and non-aromatics (naphthenes).



REFINERY SCHOOL

<https://www.youtube.com/watch?v=tpayg0dG27U>



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3.5 Crude chemistry

Fundamentally, crude oil consists of 84 – 87 wt % carbon, 11 – 14 % hydrogen, 0 – 3 wt % sulphur, 0 – 2 wt % oxygen, 0 – 0.6 wt % nitrogen and metals ranging from 0 – 100 ppm. Understanding thoroughly the fundamentals of crude chemistry is very important in various refining processes. The existence of compounds with various functional groups and their dominance or reduction in various refinery products is what is essentially targeted in various chemical and physical processes in the refinery. Based on chemical analysis and existence of various functional groups, refinery crude can be broadly categorized into about 9 categories summarized as

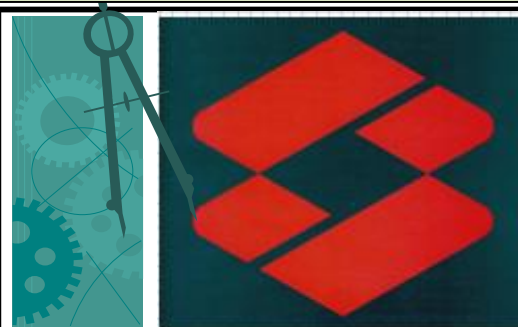
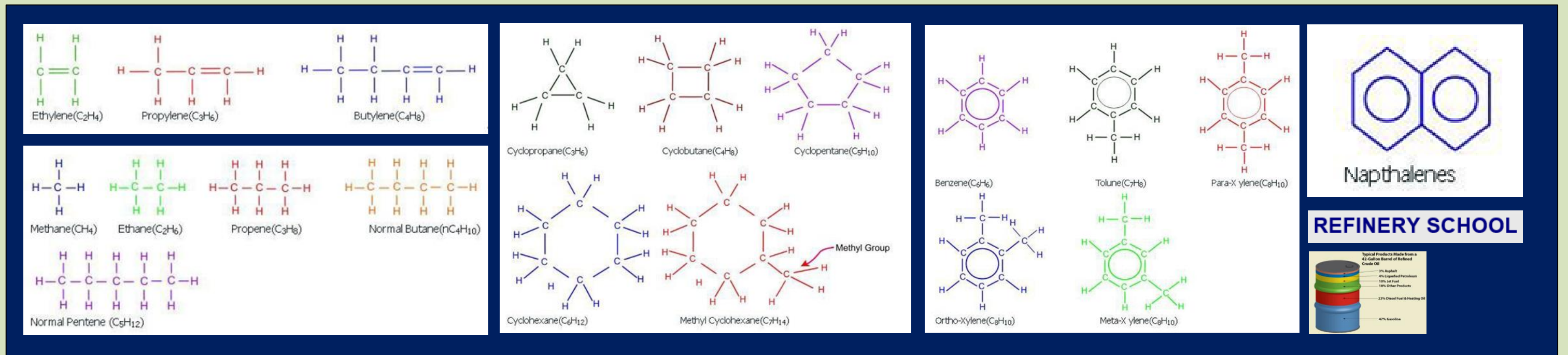
3.5.1 Paraffins: Paraffins refer to alkanes such as methane, ethane, propane, n and iso butane, n and iso pentane. These compounds are primarily obtained as a gas fraction from the crude distillation unit.

3.5.2 Olefins: Alkenes such as ethylene, propylene and butylenes are highly chemically reactive. They are not found in mentionable quantities in crude oil but are encountered in some refinery processes such as alkylation.

3.5.3 Naphthenes: Naphthenes or cycloalkanes such as cyclopropane, methyl cyclohexane are also present in the crude oil. These compounds are not aromatic and hence do not contribute much to the octane number. Therefore, in the reforming reaction, these compounds are targeted to generate aromatics which have higher octane numbers than the naphthenes.

3.5.4 Aromatics: Aromatics such as benzene, toluene o/m/p-xylene are also available in the crude oil. These contribute towards higher octane number products and the target is to maximize their quantity in a refinery process.

3.5.1 Naphthalenes: Polynuclear aromatics such as naphthalenes consist of two or three or more aromatic rings. Their molecular weight is usually between 150 – 500.



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Organic sulphur compounds: Not all compounds in the crude are hydrocarbons consisting of hydrogen and carbon only. Organic sulphur compounds such as thiophene, pyridine also exist in the crude oil. The basic difficulty of these organic sulphur compounds is the additional hydrogen requirements in the hydrotreaters to meet the **Euro III standards**. Therefore, the operating conditions of the hydrotreaters is significantly intense when compared to those that do not target the reduction in the concentration of these organic sulphur compounds. Therefore, ever growing environmental legislations indicate technology and process development/improvement on the processing of organic sulphur compounds.

3.5.1 Oxygen containing compounds: These compounds do not exist 2 % by weight in the crude oil. Typical examples are acetic and benzoic acids. These compounds cause corrosion and therefore needs to be effectively handled.

3.5.2 Resins: Resins are polynuclear aromatic structures supported with side chains of paraffins and small ring aromatics. Their molecular weights vary between 500 – 1500. These compounds also contain sulphur, nitrogen, oxygen, vanadium and nickel.

3.5.3 Asphaltenes: Asphaltenes are polynuclear aromatic structures consisting of 20 or more aromatic rings along with paraffinic and naphthenic chains. A crude with high quantities of resins and asphaltenes (heavy crude) is usually targeted for coke production.

3.6 Technical Questions:

1. 3.6.1 Explain how crude quality affects the topology of refinery configuration?

A: This is a very important question. Usually, refinery crudes are characterized as light, moderate and heavy crudes. Light and moderate crudes are typically targeted for gas, naphtha, diesel, light and heavy gas oil fractions. Heavy crudes are targeted for coke and residue product streams. Therefore, the crude quality does affect the topology of the refinery configuration. According to the choice of the crude available, refineries are classified into four types namely

- a) Those that target fuels. This is very prominent in a country like India
- b) Those that target coke. This is very much targeted for refineries that supply coke as an important raw materials to other industries such as steel, catalysts etc.
- c) Lubricants.
- d) Petrochemicals.

According to the desired product palletete, the refinery configuration and hence topology is affected with the crude quality.

2. 3.6.2 What is the basic difference between a chemical and a refinery process?

A: A chemical process essentially involves streams whose composition is fairly known. As far as refinery processes are concerned, their chemical constituents are not exactly known but are estimated as functions of various measurable properties such as viscosity, cetane number, octane number, flash point, TBP/ASTM distillation etc.

Therefore, refinery process technology should accommodate the details pertaining to these issues in addition to the technology issues.

1. 3.6.3 Why are refinery process flow sheets very complex?

A: Well, large refineries involve the production of about 30 to 40 refinery products with diverse specifications and needs of the consumers. And necessarily all these products are derived from the crude oil in a complex way. Due to complicated physical and chemical processes that are sequentially applied for various refinery process streams, refinery process flow sheets are very complex.

2. 3.6.4 How to analyze refinery process flow sheets in a simple way?

Identify

- a) Functional role of each process/operation
 - b) Plausible changes in property characteristics such as octane number or viscosity etc.
- This way refinery technology will be easy to understand with maturity.

3. 3.6.5 Relate the important crude oil cuts and associated products

- a. Gases
 - Fuel gas/LPG
- b. Naphtha
 - a. Gasoline
 - b. Jet fuel
- c. Kerosene
 - a. Jet fuel
 - b. Kerosene
- d. Light gas oil
 - a. Auto Diesel
 - b. Tractor Diesel
 - c. Home heating oil
- e. Heavy gas oil
 - a. Commercial heating oil
 - b. Industrial heating oil
 - c. Lubricants
- f. Residues
 - a. Bunker oil
 - b. Asphalt
 - c. Coke



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OVERVIEW OF A REFINERY PROCESS-CRUDE OIL AND VACUUM DISTILLATION

4.1 Introduction

In this study, a brief overview of various refinery processes is presented along with a simple sketch of the process block diagram of a modern refinery. The sketch of the modern refinery indicates the underlying complexity and the sketch is required to have a good understanding of the primary processing operations in various sub-processes and units.

4.2 Refinery flow sheet

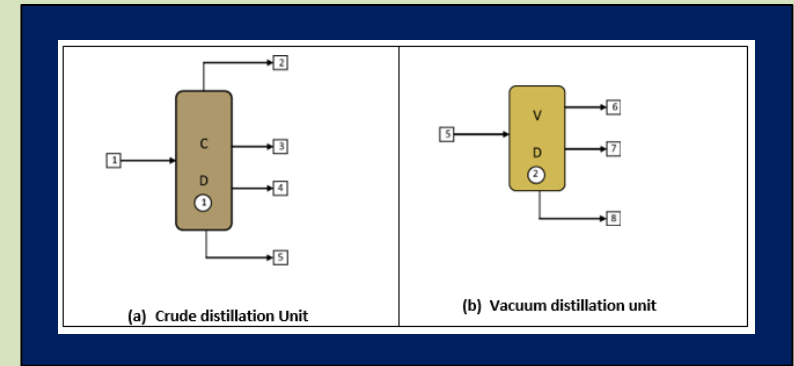
We now present a typical refinery flowsheet for the refining of middle eastern crude oil. There are about 22 units in the flowsheet which themselves are complex enough to be regarded as process flow sheets. Further, all streams are numbered to summarize their significance in various processing steps encountered in various units. However, for the convenience of our understanding, we present them as units or blocks which enable either distillation in sequence or reactive transformation followed by distillation sequences to achieve the desired products. A brief account of the above process units along with their functional role is presented next with simple conceptual block diagrams representing the flows in and out of each unit.

a) Crude distillation unit

The unit comprising of an atmospheric distillation column, side strippers, heat exchanger network, feed de-salter and furnace as main process technologies enables the separation of the crude into its various products. Usually, five products are generated from the CDU namely gas + naphtha, kerosene, light gas oil, heavy gas oil and atmospheric residue (**Figure 4.1a**). In some refinery configurations, terminologies such as gasoline, jet fuel and diesel are used to represent the CDU products which are usually fractions emanating as portions of naphtha, kerosene and gas oil. Amongst the crude distillation products, naphtha, kerosene have higher product values than gas oil and residue. On the other hand, modern refineries tend to produce lighter components from the heavy products. **Therefore, reactive transformations (chemical processes) are inevitable to convert the heavy intermediate refinery streams into lighter streams.**

Operating Conditions : The temperature at the entrance of the furnace where the crude enters is 200 – 280oC. It is then further heated to about 330 – 370oC inside the furnace. The pressure maintained is about 1 barg.

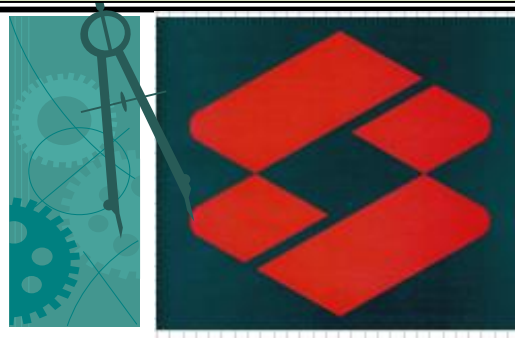
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The 22 units presented in the refinery process diagram are categorized as

- Crude distillation unit (CDU)
- Vacuum distillation unit (VDU)
- Thermal cracker
- Hydrotreaters
- Fluidized catalytic cracker
- Separators
- Naphtha splitter
- Reformer
- Alkylation and isomerisation
- Gas treating
- Blending pools
- Stream splitters

1-SEPARATION PROCESS		
111	1	ATMOSPHERIC DISTILLATION
112	2	VACUUM DISTILLATION
113	3	LIGHT ENDS RECOVERY
2-PETROLEUM CONVERSION PROCESS		
121	1	CRACKING-TERMAL AND CATALYTIC
122	2	REFORMING
123	3	ALKYLATION
124	4	POLYMERIZATION
125	5	ISOMERISATION
126	6	COKING
127	7	VISBREAKING
3-PETROLEUM TRATING PROCESSES		
131	1	HYDRODESULFURIZATION UNIT
132	2	HYDROTREATING
133	3	CHEMICAL SWEETINING
134	4	ACID GAS REMOVAL
135	5	DEASPHALTING
4-FEEDSTOCK AND PRODUCT HANDLING		
141	1	STORAGE
142	2	BLENDING
143	3	LOADING
144	4	UNLOADING
5-AUXILARY FACILITIES		
151	1	BOILERS
152	2	WASTE WATER TREATMENT
153	3	HYDROGEN PRODUCTION
154	4	SULPHUR RECOVERY PLANT
155	5	COOLING TOWERS
156	6	BLOWDOWN SYSTEM
157	7	COMPRESSOR ENGINES



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OVERVIEW OF A REFINERY PROCESS-THERMAL CRAKER HYDRPTREATER

c) Thermal cracker

Thermal cracker involves a chemical cracking process followed by the separation using physical principles (boiling point differences) to yield the desired products. Thermal cracking yields naphtha + gas, gasoil and thermal cracked residue (**Figure 4.1c**). In some petroleum refinery configurations, thermal cracking process is replaced with delayed coking process to yield coke as one of the petroleum refinery products.

Operating Conditions : The temperature should be kept at around 450 – 500oC for the larger hydrocarbons become unstable and break spontaneously. A 2-3 bar pressure must be maintained.

e) Hydrotreaters

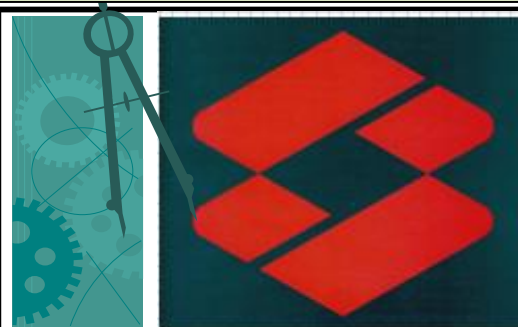
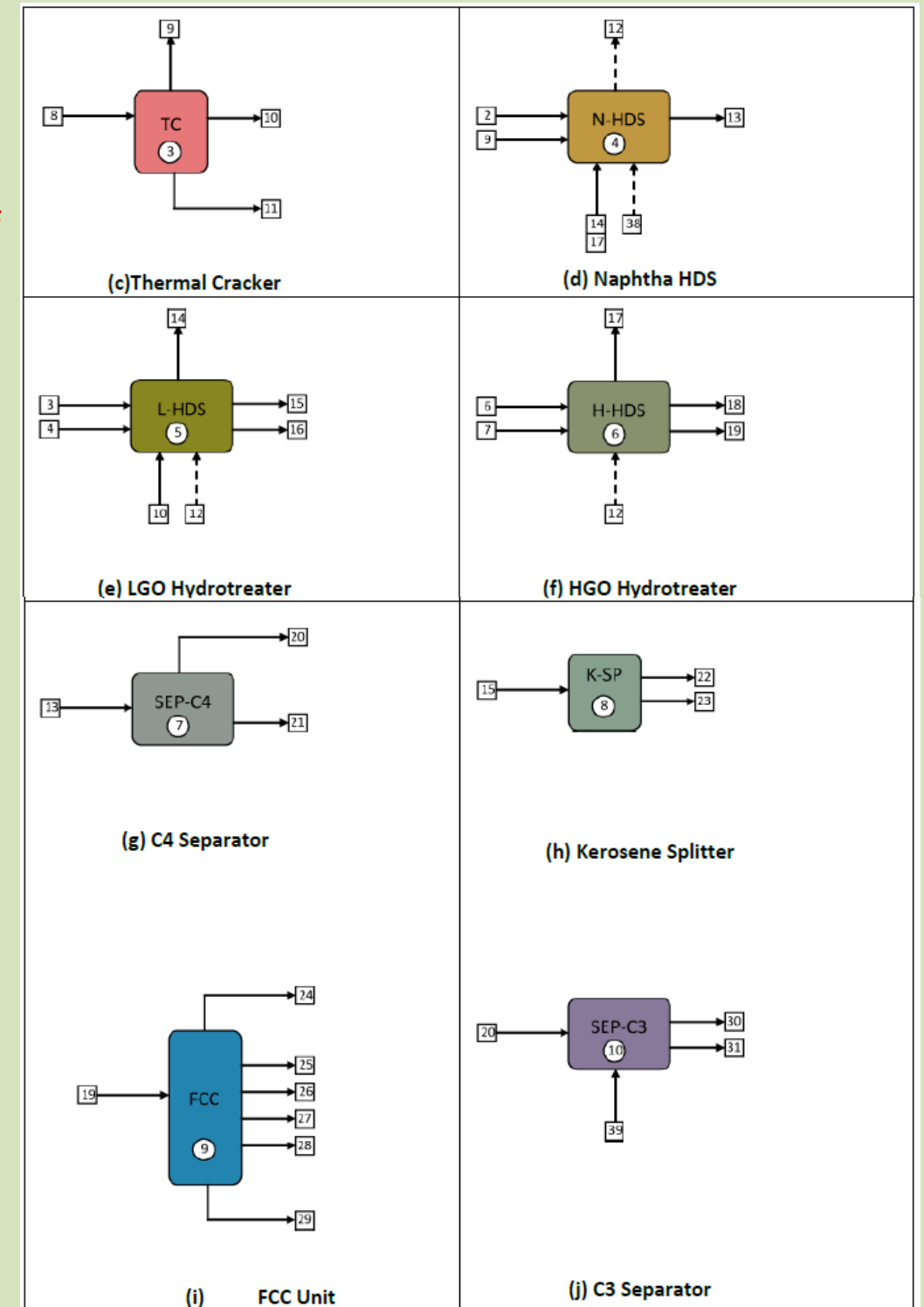
For many refinery crudes such as Arabic and Kuwait crudes, sulfur content in the crude is significantly high. Therefore, the products produced from CDU and VDU consist of significant amount of sulfur. Henceforth, for different products generated from CDU and VDU, sulfur removal is accomplished to remove sulfur as H2S using Hydrogen. The H2 required for the hydrotreaters is obtained from the reformer unit where heavy naphtha is subjected to reforming to yield high octane number reforme product and reformer H2 gas. In due course of process, H2S is produced. Therefore, in industry, to accomplish sulfur removal from various CDU and VDU products, various hydrotreaters are used. In due course of hydrotreating in some hydrotreaters products lighter than the feed are produced. For instance, in the LVGO/HVGO hydrotreater, desulfurization of LVGO & HVGO (diesel) occurs in two blocked operations and desulfurized naphtha fraction is produced along with the desulfurized gas oil main product (Figure 4.1 f). Similarly, for LGO hydrotreating case, along with diesel main product, naphtha and gas to C5 fraction are obtained as other products (**Figure 4.1e**). Only for kerosene hydrotreater, no lighter product is produced in the hydrotreating operation. It is further interesting to note that naphtha hydrotreater is fed with both light and heavy naphtha as feed which is desulfurized with the reformer off gas. In this process, light ends from the reformer gas are stripped to enhance the purity of hydrogen to about 92

% (**Figure 4.1d**). Conceptually, hydrotreating is regarded as a combination of chemical and physical processes.

Operating Conditions: The operating conditions of a hydrotreater varies with the type of feed.

For Naphtha feed, the temperature may be kept at around 280-425oC

and the pressure be maintained at 200 – 800 psig.



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OVERVIEW OF A REFINERY PROCESS-FCC AND GAS TREATING

i) Fluidized catalytic cracker

The unit is one of the most important units of the modern refinery. The unit enables the successful transformation of desulfurized HVGO to lighter products such as unsaturated light ends, light cracked naphtha, heavy cracked naphtha, cycle oil and slurry (**Figure 4.1i**). Thereby, the unit is useful to generate more lighter products from a heavier lower value intermediate product stream. Conceptually, the unit can be regarded as a combination of chemical and physical processes. **Operating Conditions: The temperature should be maintained at 340C**

with pressure ranging from 75 kPa to 180 kPa. Moreover, the process is to be carried out in a relatively wet environment.

g) Separators

The gas fractions from various units need consolidated separation and require stage wise separation of the gas fraction. For instance, C4 separator separates the desulfurized naphtha from all saturated light ends greater than or equal to C4s in composition (**Figure 4.1g**). On the other hand, C3 separator separates butanes (both iso and nbutanes) from the gas fraction (**Figure 4.1j**). The butanes thus produced are of necessity in isomerization reactions, LPG and gasoline product generation. Similarly, the C2 separator separates the saturated C3 fraction that is required for LPG product generation (**Figure 4.1k**) and generates the fuel gas + H2S product as well. All these units are conceptually regarded as physical processes. **Operating Conditions: Most oil and gas separators operate in the pressure range of 20 – 1500 psi.**

n) Naphtha splitter

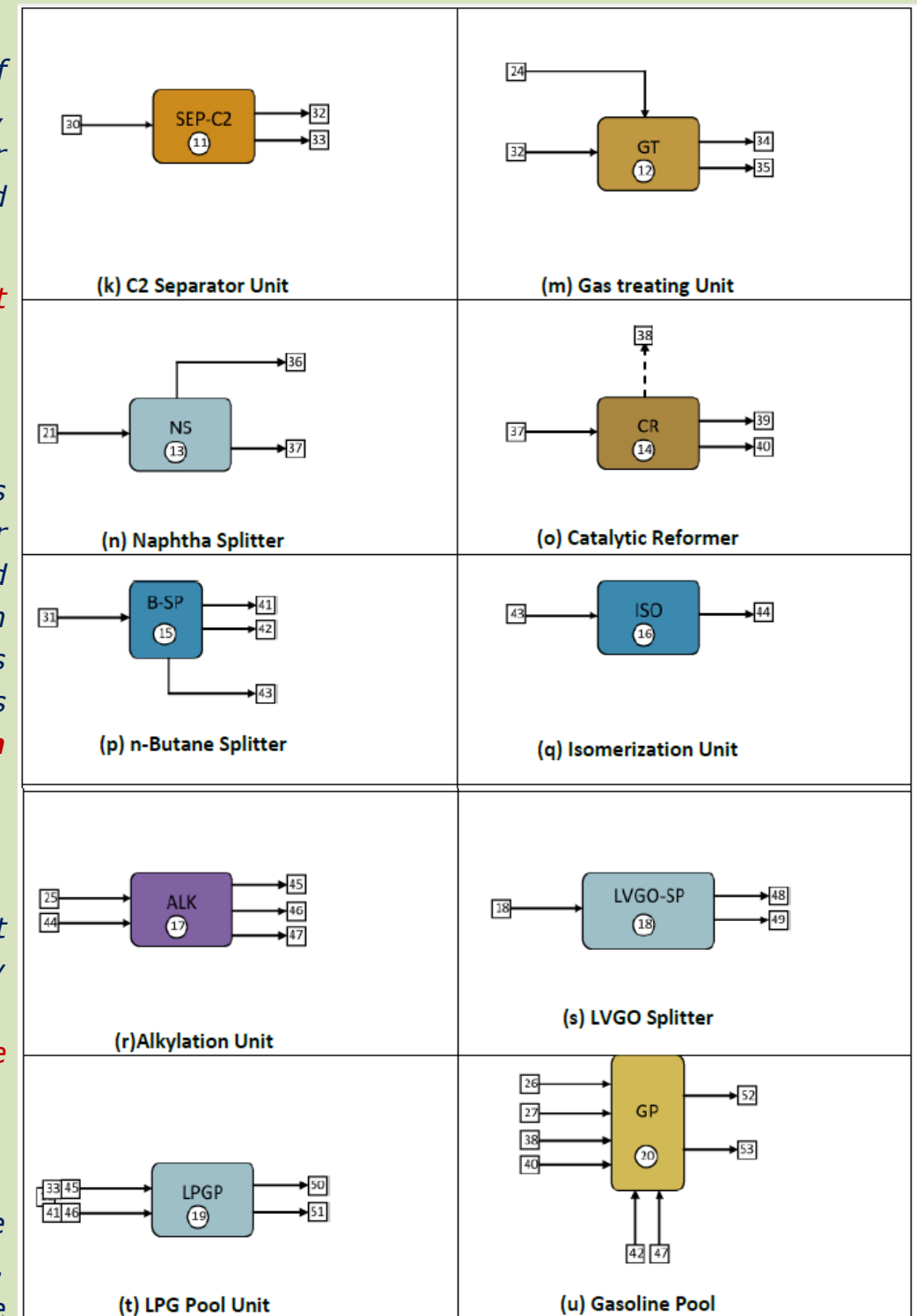
The naphtha splitter unit consisting of a series of distillation columns enables the successful separation of light naphtha and heavy naphtha from the consolidated naphtha stream obtained from several sub-units of the refinery complex (**Figure 4.1n**). The naphtha splitter is regarded as a physical process for modeling purposes.

Operating Conditions: The pressure is to be maintained between 1 kg/cm2 to 4.5 kg/cm2. The operating temperature range should be 167 – 250oC

d) Reformer

As shown in **Figure 4.1o**, Heavy naphtha which does not have high octane number is subjected to reforming in the reformer unit to obtain reformate product (with high octane number), light ends and reformer gas (hydrogen). Thereby, the unit produces high octane number product that is essential to produce premium grade gasoline as one of the major refinery products. A reformer is regarded as a combination of chemical and physical processes.

Operating Conditions : The initial liquid feed should be pumped at a reaction pressure of 5 – 45 atm, and the preheated feed mixture should be heated to a reaction temperature of 495 – 520oC.



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OVERVIEW OF A REFINERY PROCESS-ALKYLATION AND GAS TREATING

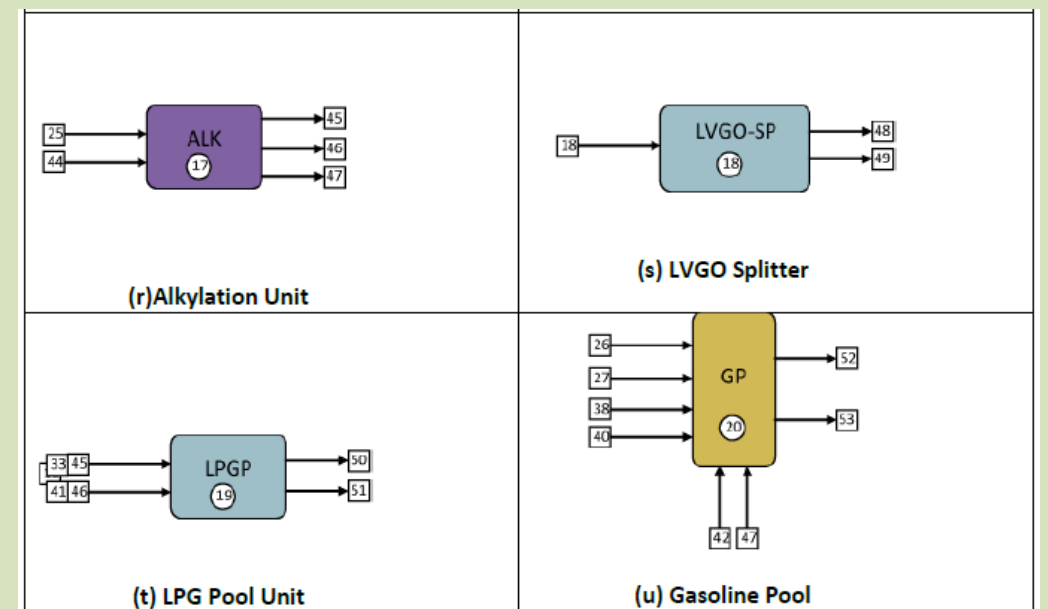
a) Alkylation & Isomerization

The unsaturated light ends generated from the FCC process are stabilized by alkylation process using iC4 generated from the C4 separator. The process yields alkylate product which has higher octane number than the feed streams (**Figure 4.1r**). As isobutane generated from the separator is enough to meet the demand in the alkylation unit, isomerization reaction is carried out in the isomerization unit (**Figure 4.1q**) to yield the desired make up iC4.

b) Gas treating

The otherwise not useful fuel gas and H2S stream generated from the C2 separator has significant amount of sulfur. In the gas treating process, H2S is successfully transformed into sulfur along with the generation of fuel gas (**Figure 4.1m**). Eventually, in many refineries, some fuel gas is used for furnace applications within the refinery along with fuel oil (another refinery product generated from the fuel oil pool) in the furnace associated to the CDU.

Operating Conditions: Gas treaters may operate at temperatures ranging from 150 psig (low pressure units) to 3000 psig (high pressure units).



a) Blending pools

All refineries need to meet tight product specifications in the form of ASTM temperatures, viscosities, octane numbers, flash point and pour point. To achieve desired products with minimum specifications of these important parameters, blending is carried out. There are four blending pools in a typical refinery. While the LPG pool allows blending of saturated C3s and C4s to generate C3 LPG and C4 LPG, which do not allow much blending of the feed streams with one another (**Figure 4.1t**). The most important blending pool in the refinery complex is the gasoline pool where in both premium and regular gasoline products are prepared by blending appropriate amounts of n-butane, reformate, light naphtha, alkylate and light cracked naphtha (**Figure 4.1u**). These two products are by far the most profit making products of the modern refinery and henceforth emphasis is there to maximize their total products while meeting the product specifications. The gasoil pool (**Figure 4.1v**) produces automotive diesel and heating oil from kerosene (from CDU), LGO, LVGO and slurry. In the fuel oil pool (**Figure 4.1w**), haring diesel, heavy fuel oil and bunker oil are produced from LVGO, slurry and cracked residue.

CHUVASH REPUBLIC-NOVOCHEBOKSARSK NEFTEKHIM REFINERY, STRATEGIC FUELS BLENDING OPTIMIZATION. Includes logos for EMERSON, CAMERON, FluiMix, and TECHNICS. Text: CRUDE OIL AND PRODUCT BLENDING SOLUTIONS.

DESIGN CRITERIA-CHUVASH LIGHT BLEND CRUDE OIL. Includes a 3D rendering of a ship's cargo hold. Text: CHEBOKSARY REFINERY 2X50,000 BPSD, CHUVASH LIGHT BLEND SPECIFICATION.

a) Stream splitters

To facilitate stream splitting, various stream splitters are used in the refinery configuration. A kerosene splitter is used to split kerosene between the kerosene product and the stream that is sent to the gas oil pool (**Figure 4.1h**). Similarly, butane splitter splits the n-butane stream into butanes entering LPG pool, gasoline pool and isomerization unit (**Figure 4.1p**).

CHUVASHNEFTEKHIM ЧУВАШНЕФТЕХИМ

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OVERVIEW OF A REFINERY PROCESS-ALYKLATION AND GAS TREATING

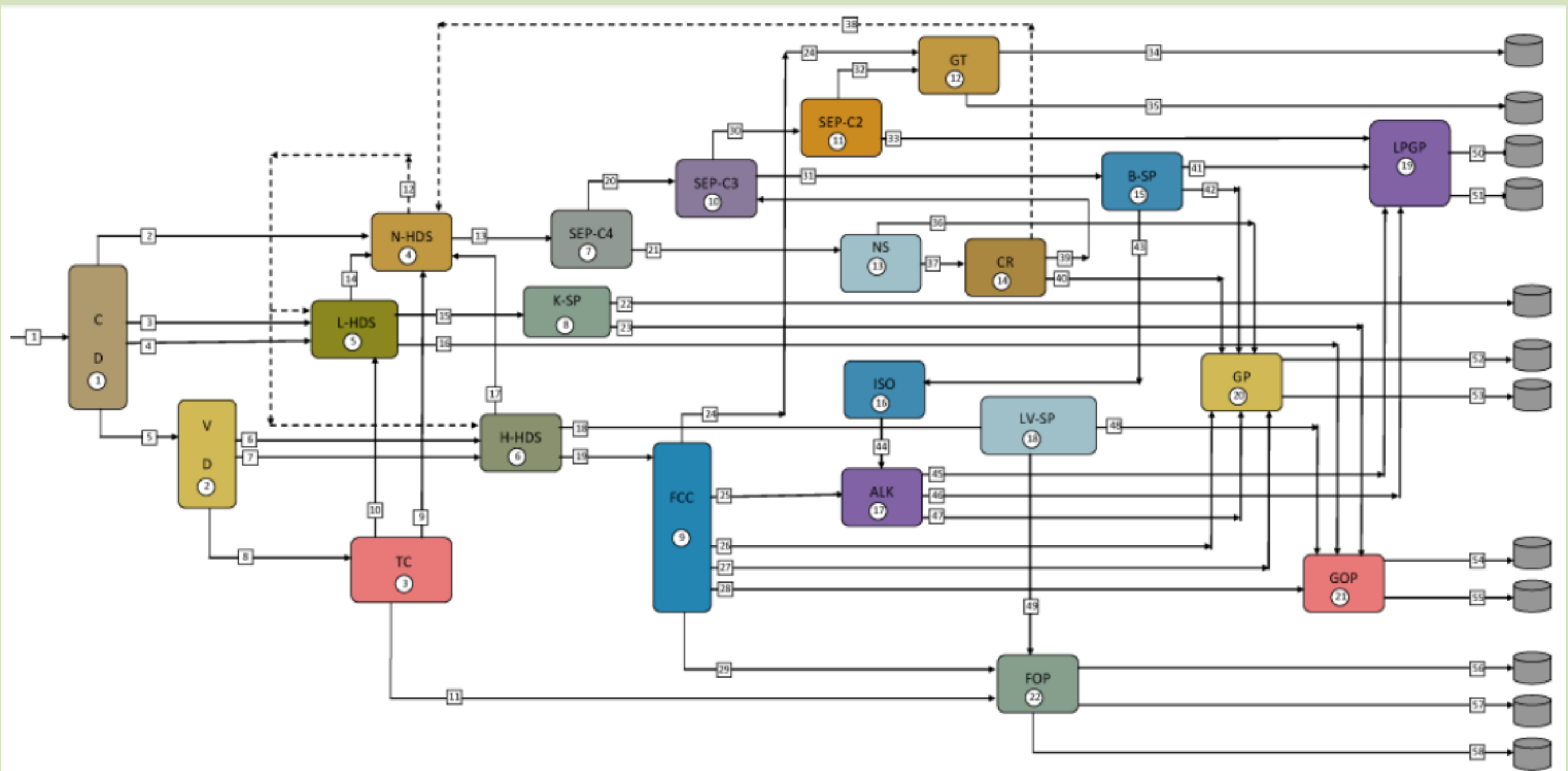


Figure 4.2: Overall refinery process block diagram (Dotted lines are for H₂ stream).



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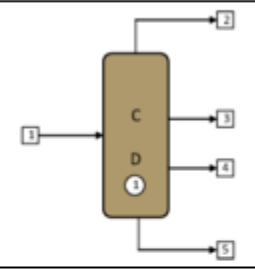
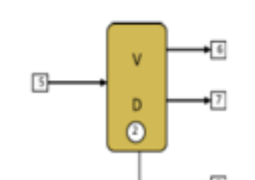
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REFINERY PROCESS-CRUDE OIL AND VACUUM DISTILLATION

LINE NO	FLUID	TIE-IN	TIE-OUT	FUNCTION
1 	CRUDE OIL	1	2	CDU-SEPERATION (BLOCK-1)
			3	N-HDS-SUPHUR REMOVAL (BLOCK-4)
			4	L-HDS, LGO HYDROTREATER
			5	L-HDS, LGO HYDROTREATER
2 	VDU	5	6	H-HDS, LIGHT VACUUM GAS OIL, SULPHUR REMOVAL
			7	H-HDS, HEAVY VACUUM GAS OIL, SULHUR REMOVAL
			8	VDU RESIDUE, TC (THERMAL CRACKING, CRACKING

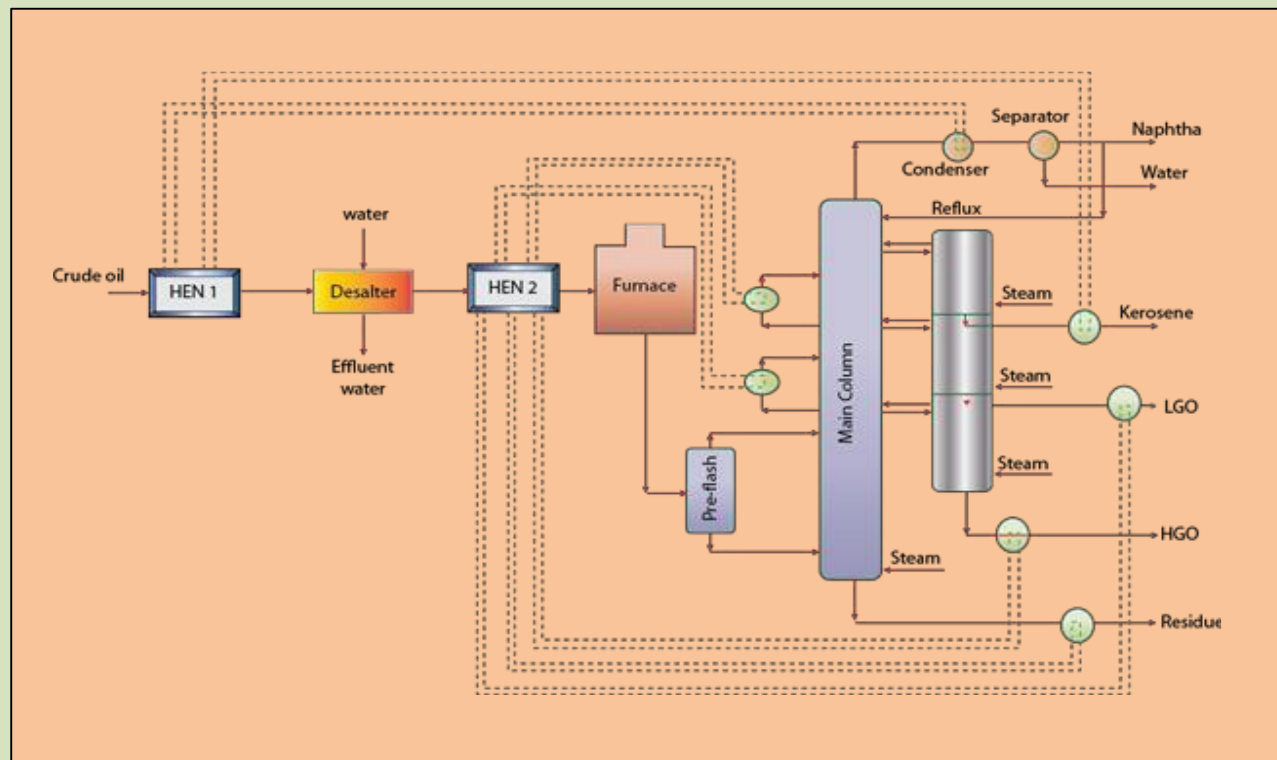
In this section, we present a brief overview of the crude distillation process.

The first essential task for the crude oil consisting of more than 108 compounds is to separate its major components based on boiling point differences. This principle is exploited in the crude distillation unit, which involves energy intensive operation. Since crude distillation involves the processing of the entire feed, it remains as the most significant operation in a refinery.

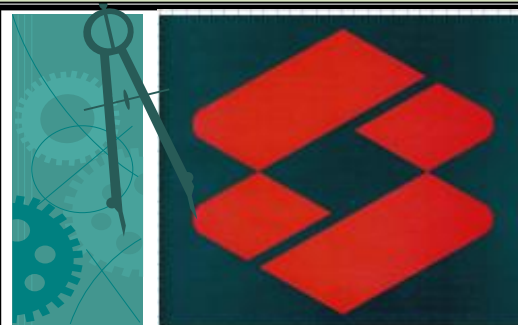
The conceptual process flowsheet for the petroleum refinery is shown in the Figure 5.1. It consists of the following important sub-processes:

- Crude desalter
 - Furnace
 - Pre-flash column
 - Crude distillation column supplemented with side columns. These columns produce the desired products
 - Pump around heat exchanger units
 - Heat exchanger network that facilitates energy recovery from hot product and reflux streams to heat the crude oil.
- Crude oil consists of dissolved salts and they tend to cause fouling and corrosion in various process equipments. Therefore, dissolved salts need to be removed using a separation process.
- The crude desalting unit is a separation process. Here, water along with other trace chemicals such as caustic and acid are allowed to enter a mixing unit along with the crude oil.


BLOCK	BLOCK FUNCTION
1	CDU-CRUDE OIL DISTILLATION UNIT
2	VDU-VACUUM DISTILLATION UNIT
3	TC-THERMAL CRACKING
4	N-HDS, NAPHTA HYDRODESULPHURIZATION UNIT
5	L-HDS, LGO HYDROTREATER
6	H-HDS, HGO HYDROTREATER
7	SEP-C4, C4 SEPERATOR
8	K-SP, KEROSENE SPLITTER
9	FCC, FLUID CATAHALYTIC CRACKER
10	SEP-C3, C3 SEPERTOR
11	SEP-C2, C2 SEPERATOR ^{II}
12	GT,GAS TREATING UNIT
13	NS, NAPHTA SPLITTER
14	CR,CATALYTIC REFORMER
15	B-SP, BUTANE SPLITTER
16	ISO,ISOMERIZATION UNIT
17	ALK,ALKYLATION UNIT
18	LVGO-SP,LVGO SPLITTER
19	LPGP,LPG POOL
20	GP,GASOLINE POOL
21	GOP,GASOIL POOL
22	FOP.FUEL OIL POOL




- The mixture of crude oil and water is subsequently passed through an electrostatic precipitator cum gravity settler. The electrostatic field enables the agglomeration of water droplets and aids faster gravity settling.
- An essential issue for the good performance of crude desalter is the temperature of the operation. Usually, high efficiency of salt removal is possible between 100 – 300 oF.
- Therefore, the crude oil is heated to about 250 oF before it enters the desalter unit.
- The clean desalted crude oil flows from the top of the gravity settler and the water along with other dissolved impurities is removed as a bottom product from the gravity settler unit.
- A high degree of salt removal is desired (95 – 99% removal of the dissolved salt in the crude oil). Usually, a two stage desalting process is deployed. When higher salt removal efficiencies are desired, three stage units are deployed.



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REFINERY PROCESS-CRUDE OIL AND VACUUM DISTILLATION

Furnace

- The furnace is an important constituent in the crude distillation unit
- Here, fuel oil and fuel gas (heavier products) obtained from the refining process itself are burnt to increase the crude oil temperature.
- Typically in refineries, the crude oil is heated to a temperature that enables overflash conditions in the main crude distillation column.
- The concept of overflash is that the crude is heated to such a temperature that enables an additional 5 % vaporization with respect to the residue product. In other words, the residue fraction vapors amounting to 5 % of the total volume of the crude oil are desired.
- Depending upon the quality of the crude, the desired temperature for the crude oil is about 600 - 700 oF.

Pre-flash column

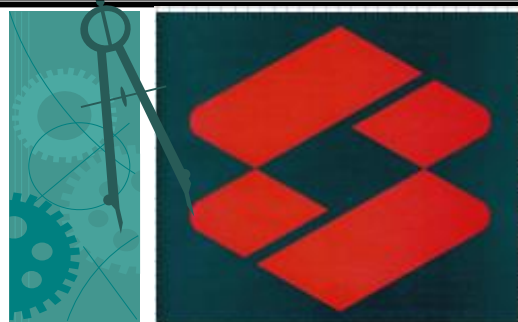
- The crude oil enters the pre-flash column after leaving the furnace
- The pre-flash tower separates the lighter fractions of the already heated crude oil.
- The heavier fractions of the crude oil leave from the bottom section of the pre- flash tower.
- Both lighter and heavier streams emanating from the pre-flash tower are fed to the main crude distillation column at various sections
- Pre-flash column enables better refluxes in the main column by distributing the streams effectively between various processing zones of the crude oil.
- Pre-flash column may or may not be included i.e., it is optional. In other words, the pre-flash column can be avoided and the heated crude oil from the furnace can be fed to the main column directly.

Main and Secondary distillation columns

- The distillation columns consisting of both main and secondary crude distillation columns are one of the most complex circuitries in distillation.
- The complex arrangement of distillation columns is based on research carried out with pilot plants and simulation software.
- The crude distillation columns (both main and primary) are regarded to an indirect sequence of thermally coupled distillation sequences to obtain the desired products.
- Effective distribution of vapor and reflux in the main column is a serious issue.
- The effective distribution of vapor and reflux is aided through pump around heat exchanger units.
- Live steam is also used in the recent designs. The live steam is usually at about 50 psig.
- The basic principle of using live steam stems out from several facts. Firstly, upon condensation, oil and water are very easy to separate. Secondly, steam can take significant amount of heat in terms of enthalpy. Thirdly, steam enables enhancement in relative volatility, a principle that is used in steam distillation laboratory experimental set ups. These principles together are anticipated to provide good dividends technically.
- Live steam cannot be just fed at one section of the CDU. It needs to be fed at various sections to ensure both good heat distribution and reduce relative volatilities of the hydrocarbons at various sections of the main and secondary towers.
- Therefore, live steam will enable good product quality as lighter hydrocarbons with higher relative volatilities in the bottom heavy product liquid streams will be easily stripped and carried along with the vapor.
- The only condenser in the main column is a partial condenser to facilitate the production of both gas and naptha+water stream.
- The circuitry totally avoided the existence of reboilers by introducing live steam. Therefore, much fixed costs of the column have been reduced. However, higher operating costs due to higher steam utilization rates are evident.

Pump-around units

- Pump around units are most essential units in the crude distillation column.
 - They are used to maintain good reflux conditions in the main column and therefore the desired product quality.
 - They also provide a good heat source as the liquid streams are at higher temperatures. Therefore, they are also important units in the heat exchanger network.
 - The cooled liquid is sent back to a section above.
 - Usually two pump arounds are used in conventional designs. However, there are crude distillation units with even three pump around units.
- The circuitry connections between primary and secondary towers along with relevant pump around units are presented in Figure5. 2. It can be seen that very complex interactions exists between the main and secondary columns.



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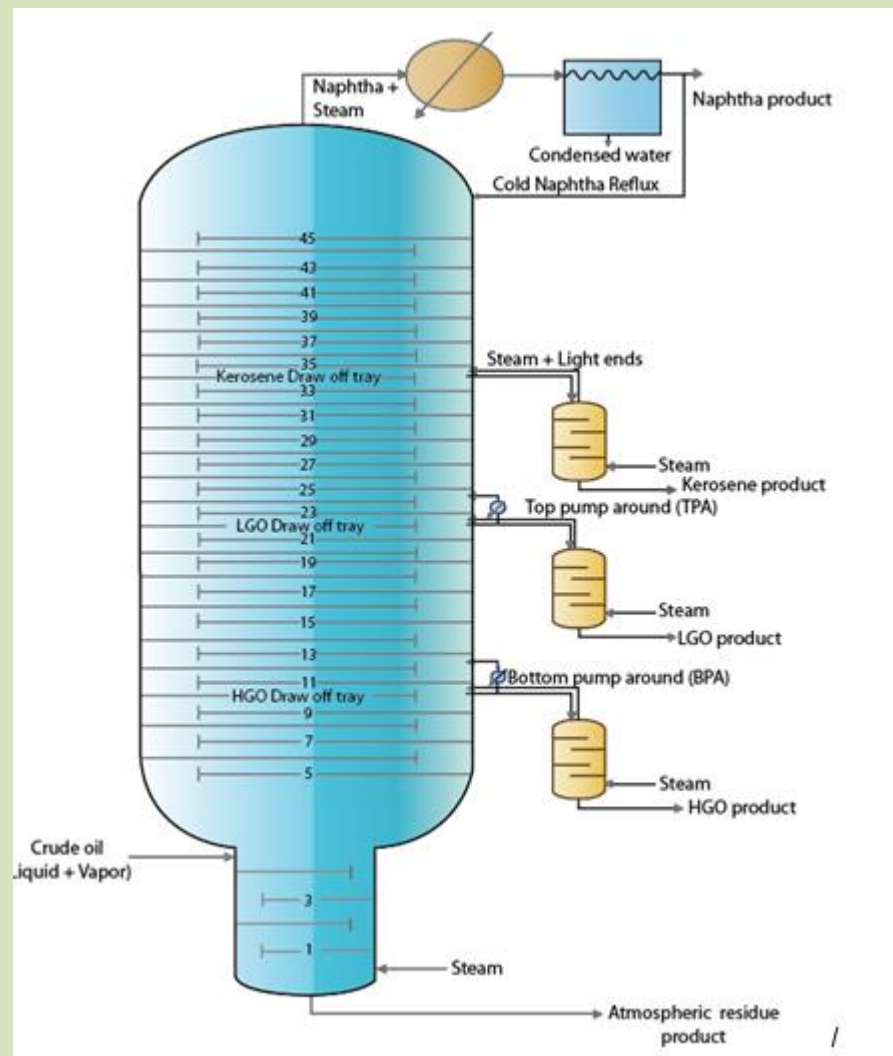
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REFINERY PROCESS-CRUDE OIL AND VACUUM DISTILLATION



- a) The main column consists of 45 trays and the secondary columns (side strippers) consist of 4 trays each. Three side strippers are used to strip the light ends from kerosene, LGO and HGO products.
- b) The main column has two sections that are distinguished with respect to a flash zone. The flash zone is where the crude oil partially vaporized is fed to the main column. There are about 4 trays below the flash zone and 41 trays above the flash zone of the main column. The bottom most tray (residue

stripping tray) is numbered as 1 and the top tower tray is numbered as 45. Trays 1 to 4 process the atmospheric residue portion of the crude in the section below the flash zone.

c) Trays 5 to 10 (6 trays above the flash zone) process the HGO product portion of the crude. From tray 10, HGO draw off product is taken out (as liquid) and enters the HGO side stripper unit. From tray 10 as well, the liquid stream is drawn and sent to tray 12 via a bottom pump around unit that enables cooling of the liquid stream. The steam + light ends from the HGO side stripper enter tray 11 of the main column.

d) Trays 13 to 22 (10 trays above the HGO processing zone) process the LGO product portion of the crude. From tray 22, LGO draw off product is taken (as liquid) and sent to the LGO side stripper unit. Also, from tray 22, another liquid stream is taken out and sent to tray 24 via a top pump around unit (TPA) that enables cooling of the liquid stream. The steam + light ends from the LGO side stripper enter tray 23 of the main column.

e) Trays 24 to 34 (10 trays above the LGO processing zone) process the kerosene product portion of the crude. From tray 34, the kero draw off stream is taken and sent to the kerosene side stripper unit. The steam + light ends of the kerosene side stripper enter tray 35.

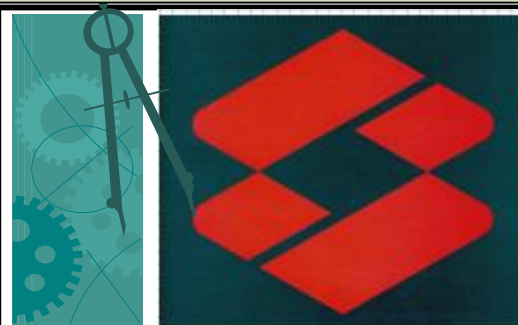
f) Trays 34 to 45 (12 trays above the Kerosene processing zone) process the naphtha product portion of the crude. **It is interesting to note that tray 34 is regarded as a tray processing both LGO as well as naphtha processing zone. This is because there is no pump around associated to the tray 34. Where pump around is associated, that tray is often ignored in counting, as it affects to a large extent the tray hydraulics and contributes less towards the separation of the components.**

g) It is interesting to note that steam enters main column at trays 1, 11, 23, 35 and therefore is present along with the vapor stream along with the hydrocarbons. Therefore, **steam balances throughout the column are very important.**

h) The cold naphtha stream obtained from the phase separator is sent back to the main column as reflux stream.

Heat exchanger networks

- Two heat exchanger networks exist in the crude distillation unit, one before the crude desalter and one after the crude desalter.
- The heat exchanger networks facilitate energy recovery from hot product, naphtha+steam vapor and reflux streams to heat the crude oil in an indirect heat transfer mode i.e, using heat exchangers.
- Therefore, the design and operation of a heat exchanger network is very important in the crude distillation unit.
- Further, it needs to be understood that the naphtha heat integrated condenser is a partial condenser where as all others are heat exchangers without any phase change streams.
- The heat exchanger networks enable to increase the crude oil stream temperature to about 200 – 230 oC which is significantly higher than the crude oil source temperature (about 20 – 30 oC).
- Crude distillation units without heat exchanger networks have higher furnace load targets. They also cause more pollution due to burning more fuel oil and fuel gas streams.



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A critical observation of the overall refinery process block diagram indicates that the straight run gasoline (this is the gasoline obtained from the CDU) does not have good octane number (40 – 60) and needs to be upgraded to obtain the desired octane number (85 – 95).

Typically, cracking, reforming and isomerisation are regarded as the three most important processes that contribute towards upgradation of the octane number.

In this lecture, we present an overview of the cracking operation in the refinery.

Typically cracking involves the thermal or catalytic decomposition of petroleum fractions having huge quantities of higher molecular weight compounds. Since heat is required, typically cracking reactions are carried out in furnaces that are supplied with either fuel oil or fuel gas or natural gas or electricity as heat source. Cracking facilitates initiation, propagation and termination reactions amongst the hydrocarbon themselves. However, when steam cracking is carried out, in addition to the energy supplied by the direct contact of steam with the hydrocarbons, steam also takes part in the reaction to produce wider choices of hydrocarbon distribution along with the generation of H₂ and CO.

6.1 What is cracking?

- Cracking involves the decomposition of heavier hydrocarbon feedstocks to lighter hydrocarbon feed stocks.
- Cracking can be carried out to any hydrocarbon feedstock but it is usually applied for vacuum gas oil (VGO)
- Cracking can be with or without a catalyst.

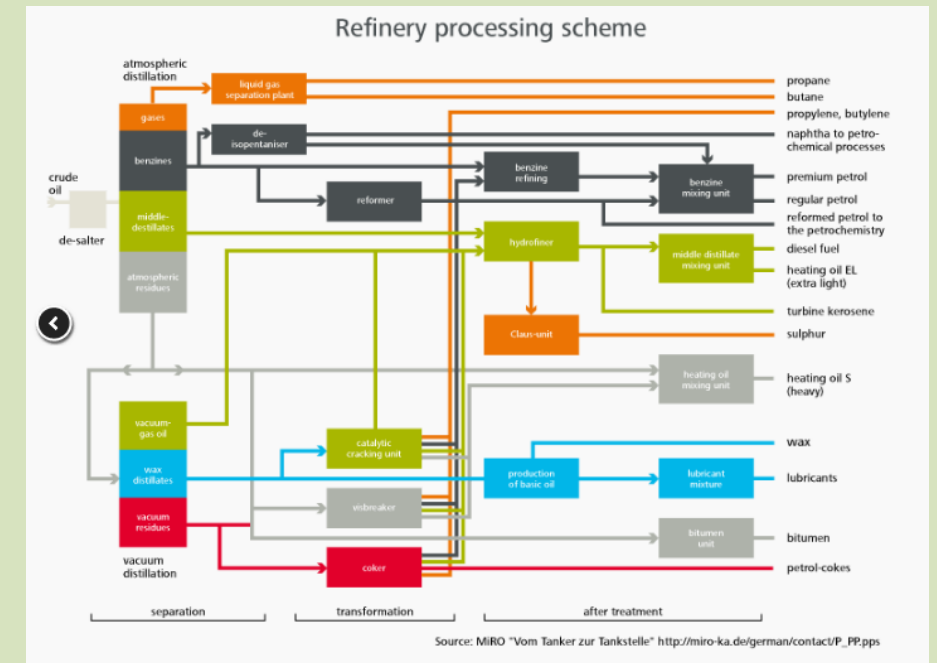
When cracking is carried out without a catalyst higher operating temperatures and pressures are required. This is called as thermal cracking. This was the principle of the old generation refineries.

- Now a days, cracking is usually carried out using a catalyst.

The catalyst enabled the reduction in operating pressure and temperature drastically.

Cracking chemistry

- Long chain paraffins converted to olefins and olefins
- Straight chain paraffins converted to branched paraffins
- Alkylated aromatics converted to aromatics and paraffins
- Ring compounds converted to alkylated aromatics
- Dehydrogenation of naphthenes to aromatics and hydrogen
- Undesired reaction: Coke formation due to excess cracking
- Cracking is an endothermic reaction



Therefore, in principle cracking generates lighter hydrocarbons constituting paraffins, olefins and aromatics. In other words, high boiling low octane number feed stocks are converted to low boiling high octane number products.

Operating conditions

- These very much depend upon the feed stock and type of cracking (thermal /catalytic) used.
- Cracking is a gas phase reaction. Therefore, entire feedstock needs to be vaporized.
- It was observed that short reaction times (to the order of 1 – 3 seconds only) provide good quality product and less coke formation.
- For vacuum gas oil, thermal cracking requires operating at 600 oC and 20 atms gauge pressure.
- For vacuum gas oil, catalytic cracking is usually carried out at 480 oC and 0.7

1 atms gauge pressure. Catalyst

- Acid treated silica-alumina was used as catalyst.
- 20 – 80 mesh size catalysts used for FCCR and 3 – 4 mm pellets used for MBRs
- During operation, poisoning occurs with Fe, Ni, Vd and Cu

LINE NO	FLUID	TIE-IN	TIE-OUT	FUNCTION
3	VDU RESIDUE	8	9	N-HDS (BLOCK-4), NAPHTHA-HDS
			10	L-HDS (BLOCK-5), LGO HYDROTREATER
			11	FOP,FUEL OIL POOL (BLOCK-22)
9	HHDS	19	24	GT,GAS TREATING,(BLOCK-12)
			25	ALK,ALKYLATION,(BLOCK-17)
			26	GP,GASOLINE POOL, (BLOCK-20)
			27	GP,GASOLINE POOL, (BLOCK-20)
			28	GOP,GASOIL POOL,(BLOCK-21)
			29	FOP,FUEL OIL POOL, (BLOCK-22)

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REFINERY PROCESS-CRACKING UNIT BASICS

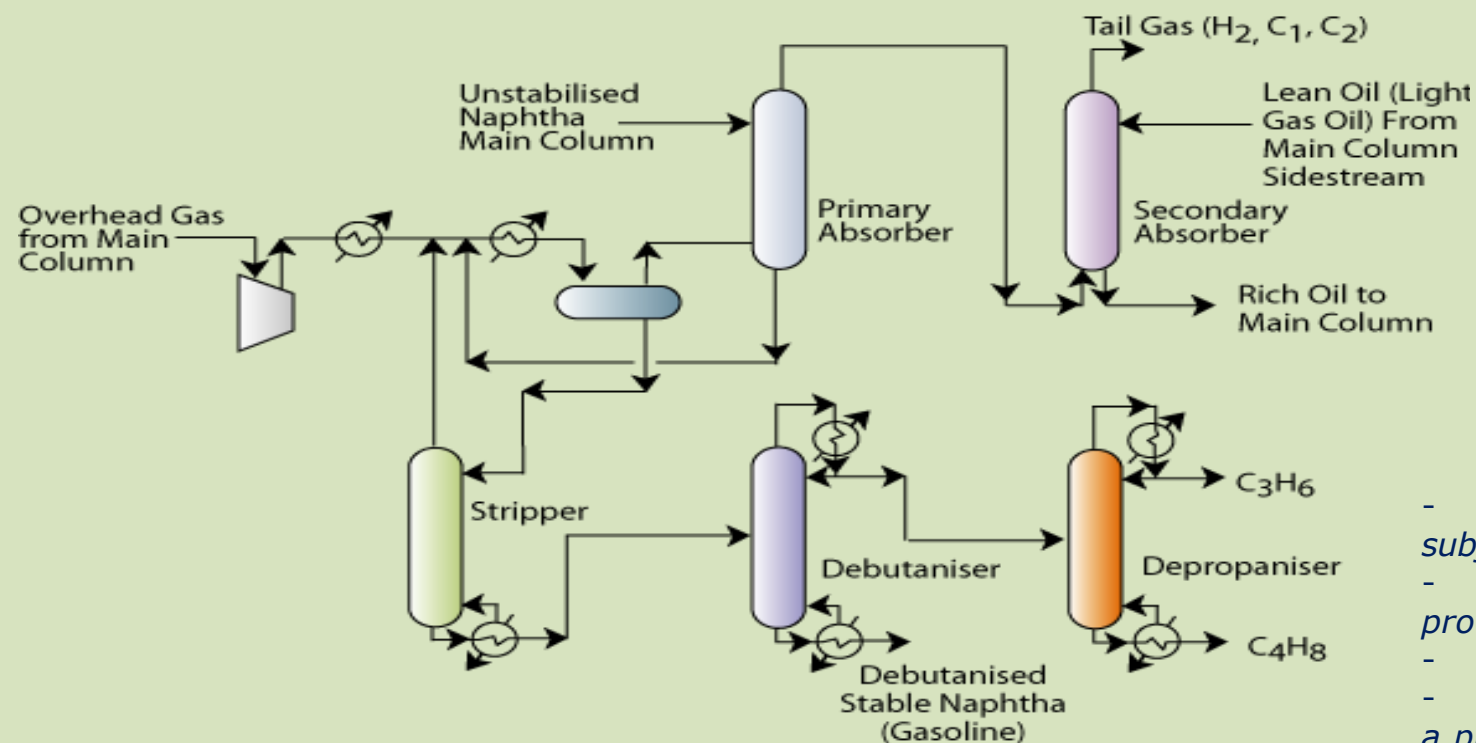
Catalyst

- Acid treated silica-alumina was used as catalyst.
- 20 – 80 mesh size catalysts used for FCCR and 3 – 4 mm pellets used for MBRs
- During operation, poisoning occurs with Fe, Ni, Vd and Cu

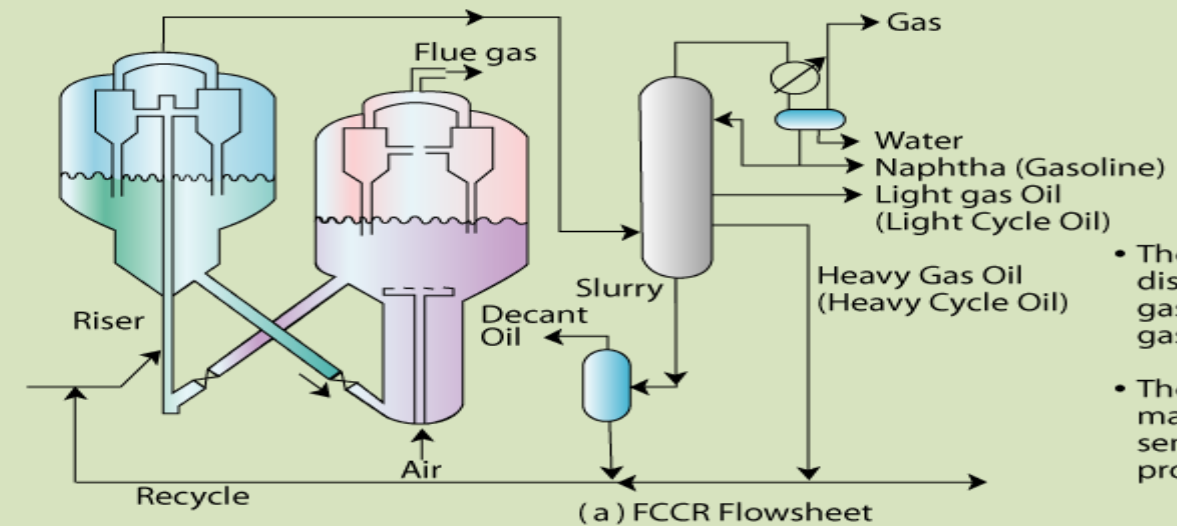
Process technology

The process technology consists of two flowsheets namely the cracking coupled with main distillation column and stabilization of naphtha.

Catalytic Cracking : Overview



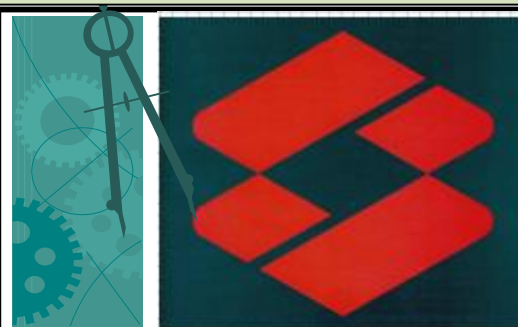
Catalytic Cracking : Overview



- The products are distilled to give light gas, gasoline and light gas oil
- The heavier products may be recycled or sent for further processing elsewhere

Flow sheet of Catalytic Cracking process

- Feed enters the cracking reactor.
- Old generation refineries used moving bed reactors
- Now a days, fluidized catalytic cracking (FCC) reactors are used.
- The cracked product from the reactor enters a main distillation column that produces unstabilized naphtha, light gas oil, heavy gas oil, slurry and gas.
- The naphtha obtained is unstabilized, as it consists of various hydrocarbons. It is therefore subjected to stabilized by continued processing.
- The slurry enters a phase separation unit which separates decant oil and a heavier product. The heavier product is recycled back to the cracking reactor.
- The unstabilized naphtha subsequently enters a unsaturates gas plant
- In the unsaturates gas plant, the gas obtained from the main distillation column is sent to a phase separator. The phase separator separates lighter hydrocarbons from heavier hydrocarbons.
- The phase separator is also fed with the unstabilized naphtha. The unstabilized naphtha from the main column is first fed to a primary absorber to absorb heavier hydrocarbons in the gas stream emanating from the phase separator. The gas leaving the primary absorber is sent to a secondary absorber where light gas oil from main distillation column is used as a absorbent to further extract any absorbable



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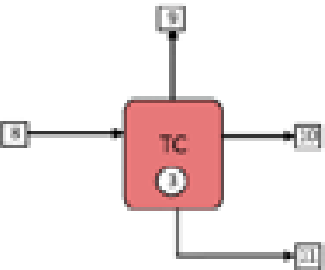
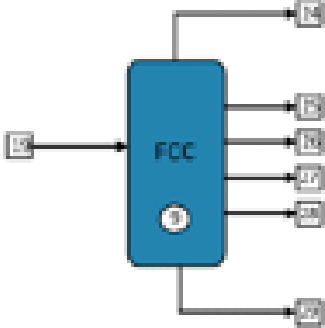
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REFINERY PROCESS-CRACKING UNIT BASICS

- hydrocarbons into the light gas oil. Eventually, the rich light gas oil enters the main distillation column (not shown in the figure a).
- The naphtha generated from the phase separator is sent to stripping to further consolidate and stabilize naphtha
- The stabilized naphtha is further subjected to distillation in debutanizer and depropanizer units
- The debutanizer unit removes butanes and lower hydrocarbons from the naphtha. The naphtha obtained as bottom product in the debutanizer is termed as debutanized stable naphtha or gasoline.
- The butanes and other hydrocarbons are sent to a depropanizer unit where butanes are separated from propanes and other lighter hydrocarbons. Thus, butanes are obtained as lower product and propanes along with other lighter hydrocarbons are obtained as the top product in the depropanizer unit.

LINE NO	FLUID	TIE-IN	TIE-OUT	FUNCTION
	VDU RESIDUE	8	9	N-HDS (BLOCK-4), NAPHTA-HDS
			10	L-HDS (BLOCK-5), LGO HYDROTREATER
			11	FOP, FUEL OIL POOL (BLOCK-22)
	HHDS	19	24	GT, GAS TREATING, (BLOCK-12)
			25	ALK, ALKYLATION, (BLOCK-17)
			26	GP, GASOLINE POOL, BLOCK-20)
			27	GP, GASOLINE POOL, BLOCK-20)
			28	GOP, GASOIL POOL, (BLOCK-21)
			29	FOP, FUEL OIL POOL, (BLOCK-22)

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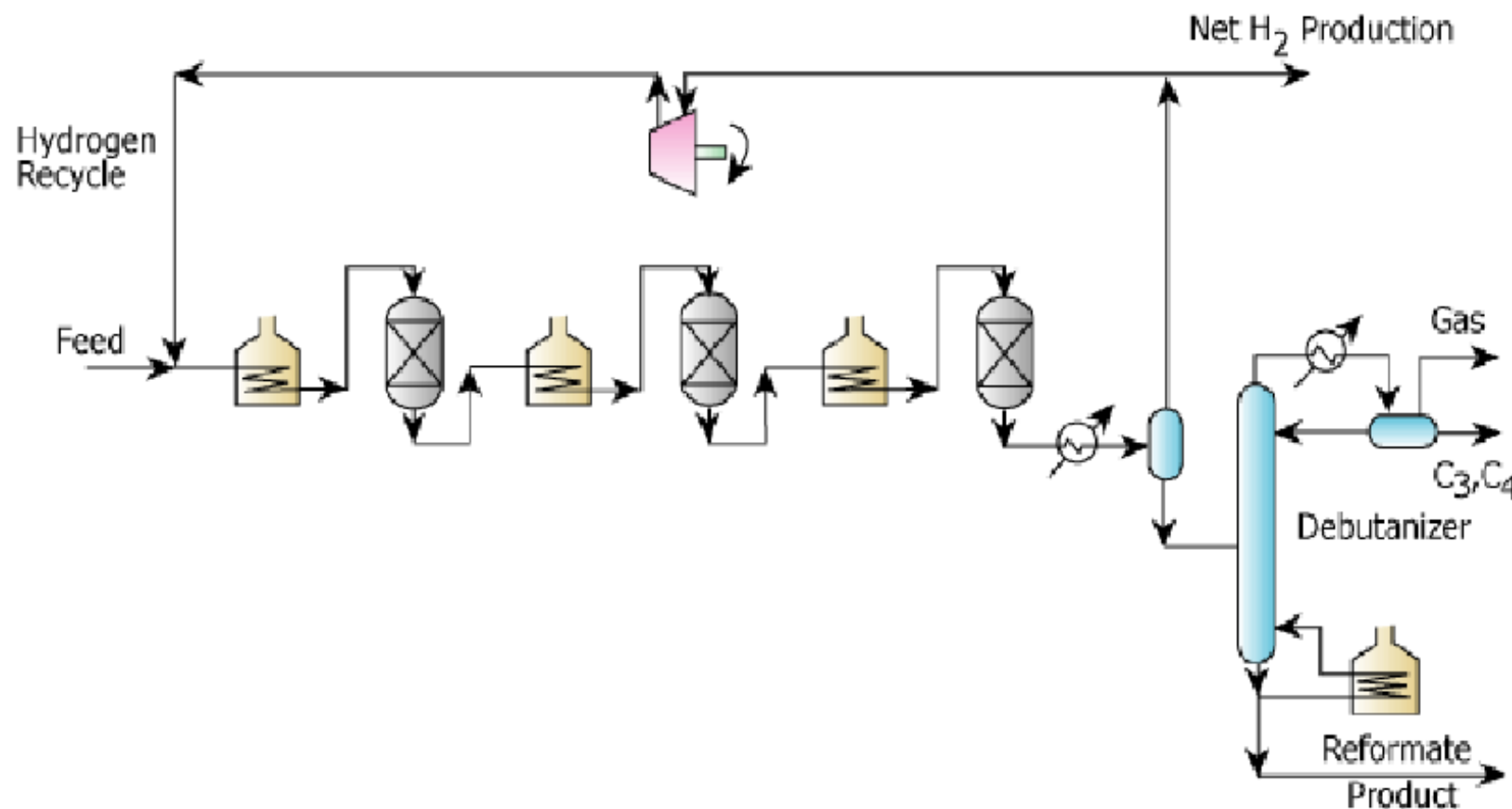
REFINERY PROCESS-REFORMING AND ISOMERIZATION UNIT BASICS

Introduction Reforming

- The catalytic cracking involves enhancing the octane number of the product
- Heavy naphthas are used are typical feed stocks
- The reaction is carried out on a catalyst
- Reforming reaction produces hydrogen as a by product which is used elsewhere in the refinery
- Usually Platinum supported on porous alumina is used as a catalyst
- Catalyst activity enhanced using chloride



Catalytic Reforming : Flowsheet

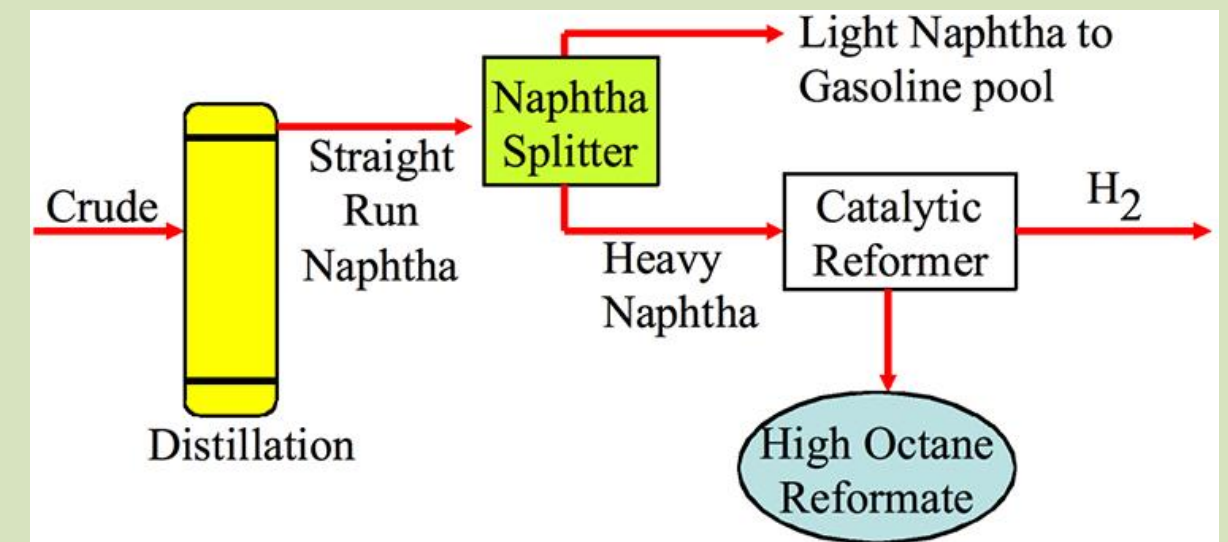


- Products from reactor cooled (often by heat exchange with feed), partially condensed to separate hydrogen-rich gas from the liquid products.
- Reformate separated from C₄- by distillation.

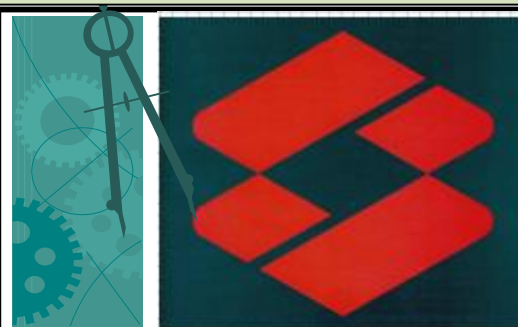
Cracking Chemistry

- Paraffin isomerisation takes place
- Naphthene isomerisation also takes place to produce cycloalkanes
- Cyclo alkanes undergo dehydrogenation to generate aromatics
- Dehydrocyclization takes place to convert side chained alkanes to cyclo alkanes and hydrogen
- In summary lower octane number feeds are converted to high octane products

The reformate thus produced has high octane and aromatics (benzene, toluene and xylene) con



- The reactions are endothermic. Therefore, heat needs to be supplied



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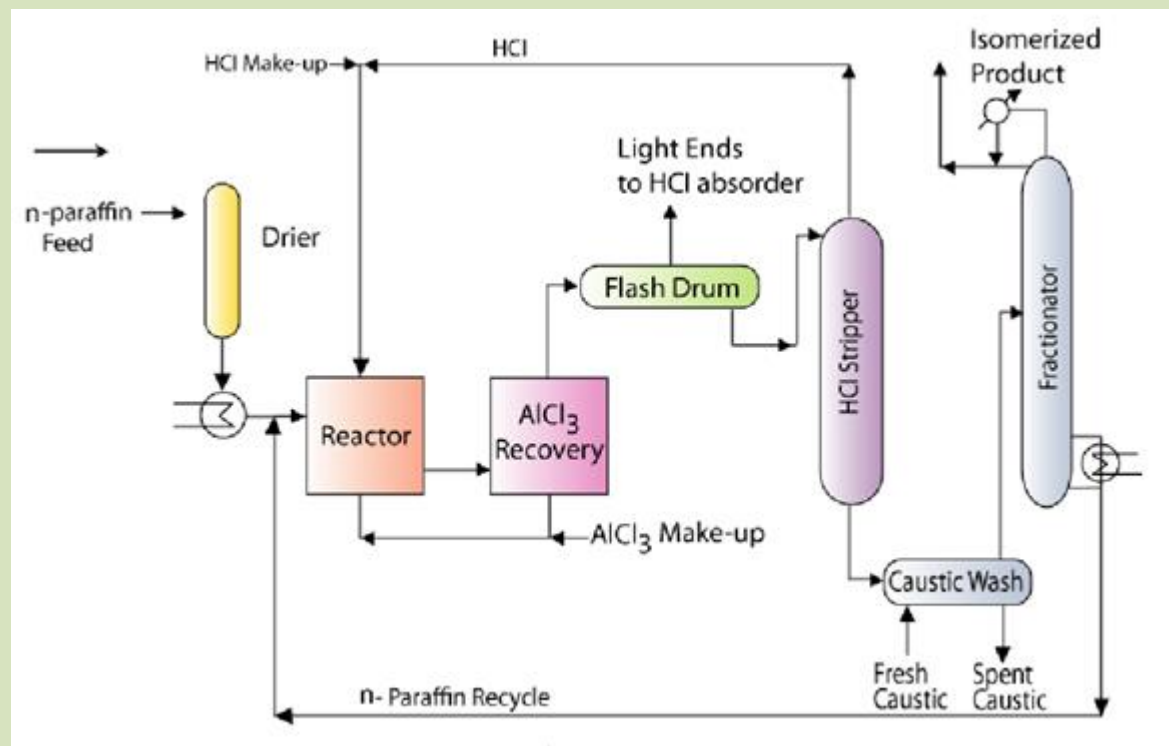
REFINERY PROCESS-REFORMING AND ISOMERIZATION UNIT BASICS

Process technology (Figure 7.1)

- The feed is mixed with recycled hydrogen
- Subsequently, it is heated before sending to reactor
- Since the reactions are highly endothermic, several combinations of reactor + heaters are used.
- The products from the final reactor are cooled. Often this is carried out with heat recovery principle in which heat is recovered using the fresh feed to the first reactor.
- After this, the product mixture enters a phase separator which separates the hydrogen gas stream from the liquid stream.
- The liquid stream from the phase separator is sent to a debutanizer distillation column that separates butanes and lower alkanes from the reformate product.
- The hydrogen produced in the phase separator is compressed and sent back to the first reactor.
- Excess hydrogen generated in the reactions is taken out as a bleed stream
- Catalyst regeneration (not shown in the flow sheet) needs to be carried out to regain catalyst activity. This can be in different modes of operation namely cyclic, semi-regenerative or continuous. When continuous mode of catalyst regeneration is carried out (as in UOP continuous catalytic reforming process), the moving bed designs are used for the reforming reactor. Additional complexity in the moving bed reactors is to enable process intensification to club the sequence of three reactors + heaters into one single unit.

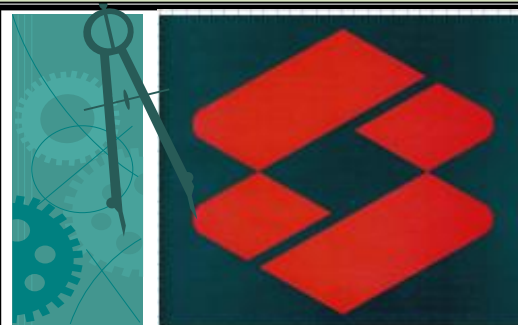
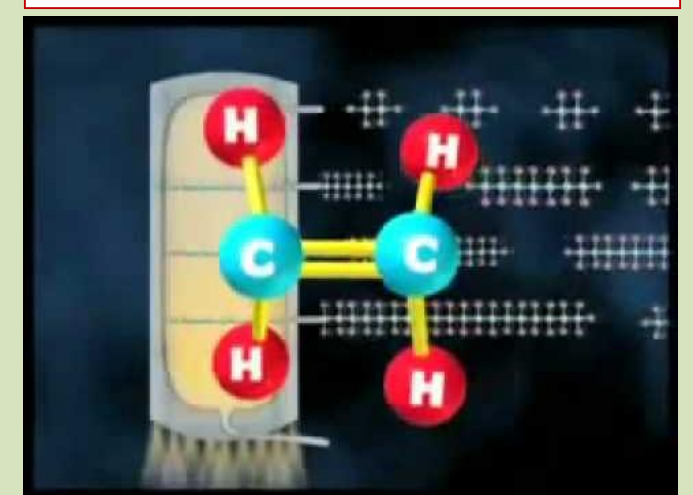
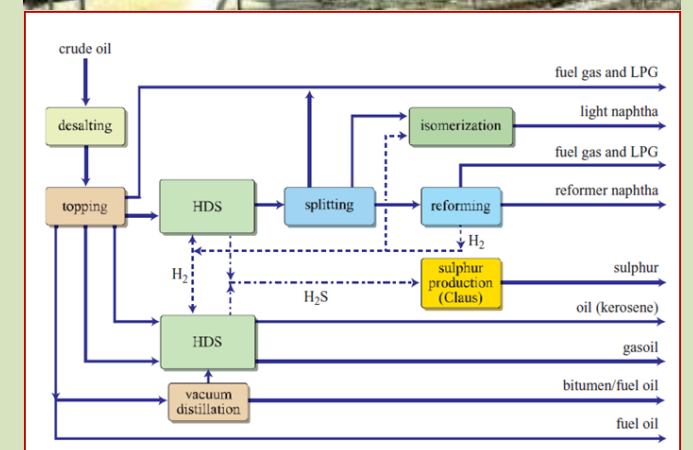
Process parameters

- Reactor pressure: 4 – 24 barg
- Reactor temperature: 500 – 525 oC
- H₂/Hydrocarbon molar ratio: 2 – 3
- The basic principle of Isomerization is to straight chain alkanes to side chain paraffins. This enhances the octane number substantially
- For instance, n-pentane has an octane number of 61.7 where as iso-pentane has an octane number of 92.3, - Usually light naphtha is used as a feed stock



Catalyst

- Platinum base catalysts are used
- AlCl₃ is used as a promoter for the catalyst
- During reaction, part of the AlCl₃ 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



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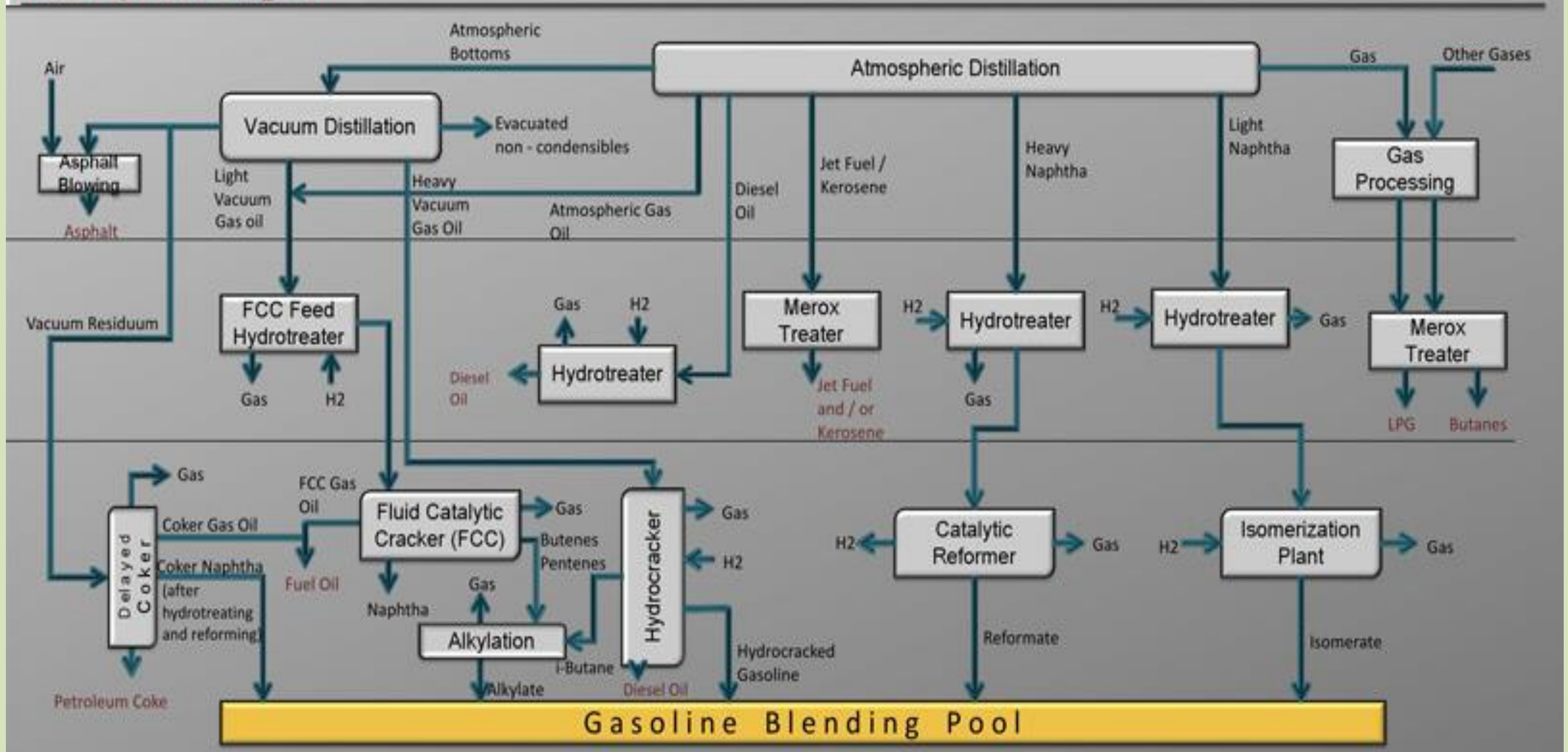
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REFINERY PROCESS-HYDRO-PRECESSING UNIT BASICS

Refinery Flow Diagram



SIMPLIFIED VERTICAL OIL REFINERY TYPICAL BLOCK DIAGRAM

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REFINERY PROCESS-HYDRO-PRECESSING UNIT BASICS

Introduction

- In this lecture, we present a brief overview of the hydroprocessing operations in the petroleum refinery. The hydroprocessing operations mainly involve hydrotreating and hydrocracking units.
- From reforming and cracking reactions, the gasoline yields have been predominantly increased. However, their quality has not been addressed.
- Gasoline and other products from intermediate operations have good number of undesired materials.
- The undesired materials mainly include (a) organic sulphur containing compounds (b) organic nitrogen containing compounds and (c) metals.
- Other undesired materials include olefins (double bond compounds) and metals.
- The sulphur removal from various refinery intermediate process streams is desired for several reasons. Firstly, the fuel specifications with lower sulphur content should be met. Secondly, the shelf life of sulphur sensitive platinum catalysts need to be increased.
- Similarly, nitrogen removal from various process streams is desired to improve yields, reduce catalyst poisoning, reduce NOx formation in combustion etc.
- The metals such as Vanadium and Nickel need to be removed as they tend to poison the catalyst and can cause environmental problems after combustion.
- The olefin removal is primarily desired to obtain clean products after combustion. Other than this, the formation of polymeric (gum type) compounds in fuel combustion be avoided.
- Aromatics removal is desired primarily to meet the desired specifications.

Definitions of hydroprocessing, hydrotreating and hydrocracking

- In hydroprocessing, feedstocks are sent to a catalytic reactor in the presence of hydrogen.
- Depending upon the intensity of the hydroprocessing operation, the hydroprocessing is termed as hydrotreating or hydrocracking.
- During hydrotreating, sulphur and nitrogen concentration in the final products is reduced along with the saturation of olefins and aromatics. However, boiling range of the final products will be similar to that of the feed stock.
- During hydrocracking, heavier molecules react with hydrogen to generate lighter hydrocarbons.

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**Hydrotreating
Introduction**

REFINERY PROCESS-HYDRO-PRECESSING UNIT BASICS

- In hydrotreating, sulphur, nitrogen and metals removal is targeted along with the saturation of olefins and aromatics. Thus the operating conditions of the hydrotreater unit will be the same for the simultaneous removal of S, N & O as H₂S, NH₃, H₂O respectively. These products will be separated in the off gas and the off gas will be further subjected to gas treating.
- The boiling point range of the products is not significantly different from that of the feedstocks.
- From chemistry perspective, inorganic sulphur is converted to H₂S. Organic sulphur compounds such as mercaptans, sulphides, disulphides, thiophenes are converted to corresponding saturated hydrocarbons along with the generation of H₂S. Similarly, denitification reactions also take place during hydrotreating in which compounds such as pyrrole, pyridine and quinoline are converted to saturated hydrocarbons. Ammonia is generated as a byproduct in the denitrification reactions.
- The olefins are converted to both cyclic and non-cyclic saturated hydrocarbons. Similarly, aromatic hydrocarbons such as toluene, naphthalene and tetrahydronaphthalene are converted to corresponding cyclic hydrocarbon compounds. The removal of vanadium and nickel is usually difficult. This is due to the reason that they are held within asphaltene molecules and intense operating conditions (higher T, P and molar ratio of hydrogen to hydrocarbon feed) are required.

Year	Process name	Purpose	By-products, etc.
1862	Atmospheric distillation	Produce kerosene	Naphtha, tar, etc.
1870	Vacuum distillation	Lubricants (original) Cracking feedstocks (1930's)	Asphalt, residual coker feedstocks
1913	Thermal cracking	Increase gasoline	Residual, bunker fuel
1916	Sweetening	Reduce sulfur & odor	Sulfur
1930	Thermal reforming	Improve octane number	Residual
1932	Hydrogenation	Remove sulfur	Sulfur
1932	Coking	Produce gasoline basestocks	Coke
1933	Solvent extraction	Improve lubricant viscosity index	Aromatics
1935	Solvent dewaxing	Improve pour point	Waxes
1935	Cat. polymerization	Improve gasoline yield & octane number	Petrochemical feedstocks
1937	Catalytic cracking	Higher octane gasoline	Petrochemical feedstocks
1939	Visbreaking	Reduce viscosity	Increased distillate, tar
1940	Alkylation	Increase gasoline octane & yield	High-octane aviation gasoline
1940	Isomerization	Produce alkylation feedstock	Naphtha
1942	Fluid catalytic cracking	Increase gasoline yield & octane	Petrochemical feedstocks
1950	Deasphalting	Increase cracking feedstock	Asphalt
1952	Catalytic reforming	Convert low-quality naphtha	Aromatics
1954	Hydrodesulfurization	Remove sulfur	Sulfur
1956	Inhibitor sweetening	Remove mercaptan	Disulfides
1957	Catalytic isomerization	Convert to molecules with high octane number	Alkylation feedstocks
1960	Hydrocracking	Improve quality and reduce sulfur	Alkylation feedstocks
1974	Catalytic dewaxing	Improve pour point	Wax
1975	Residual hydrocracking	Increase gasoline yield from residual	Heavy residuals

22

REFINERY SITTING WORKBOOK
Appendices A & B
Published July 1988

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SCHEMATICS OF THIS STUDY HAS BEEN EXTRACTED FROM ABOVE DOCUMENT

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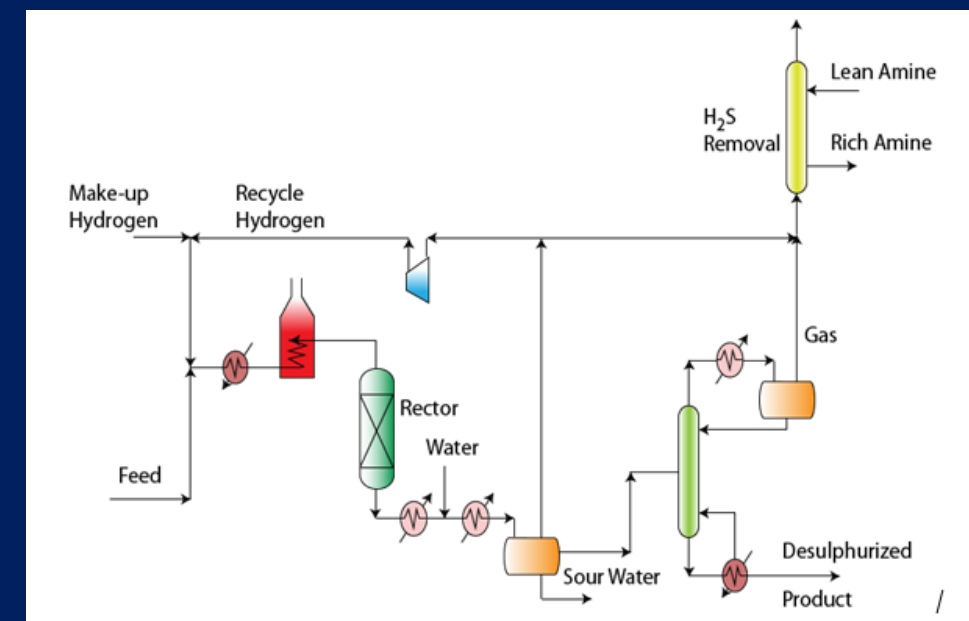
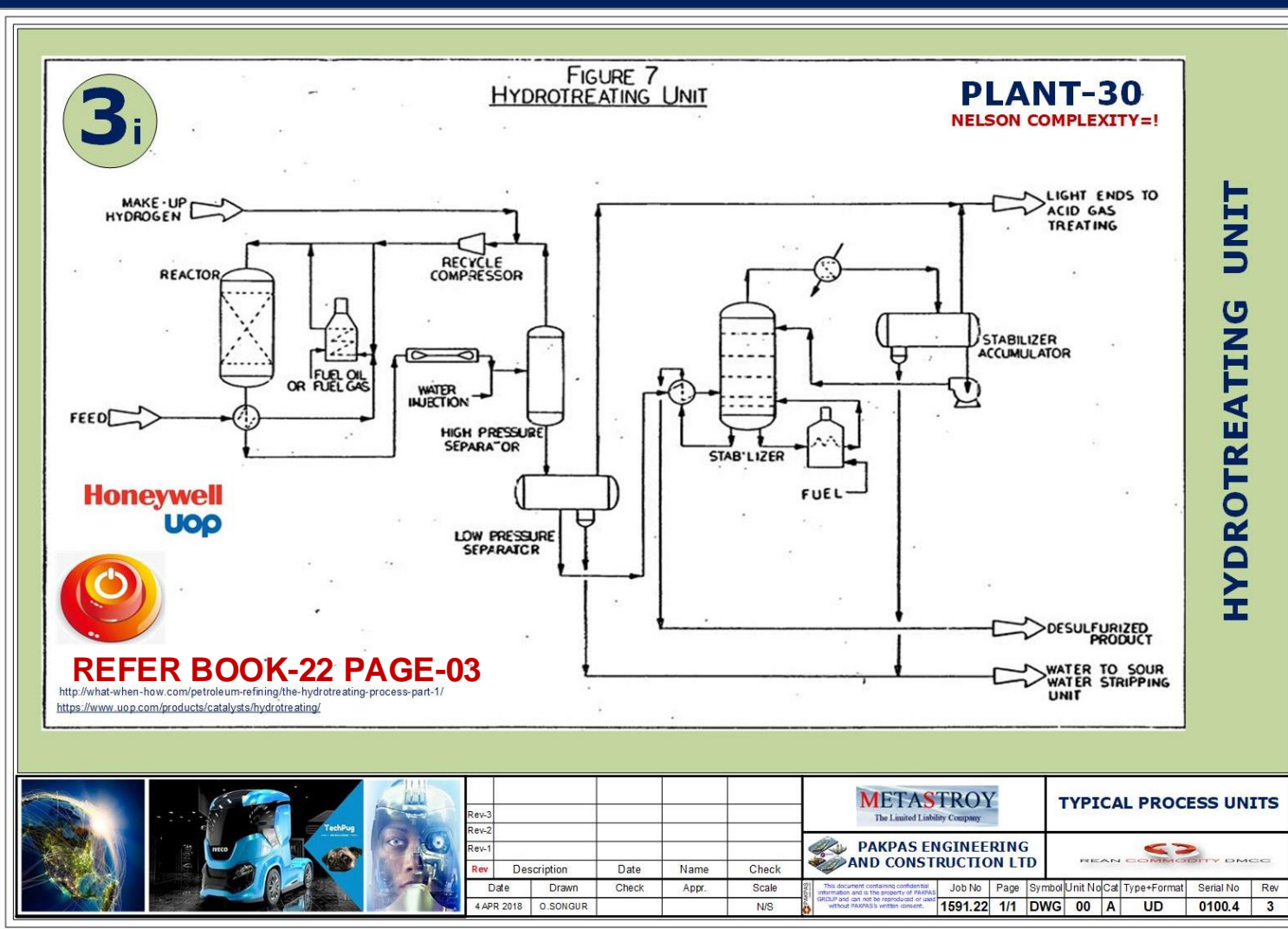
REFINERY PROCESS-HYDRO-PRECESSING UNIT BASICS

Definitions of hydroprocessing, hydrotreating and hydrocracking

- In hydroprocessing, feedstocks are sent to a catalytic reactor in the presence of hydrogen.
- Depending upon the intensity of the hydroprocessing operation, the hydroprocessing is termed as hydrotreating or hydrocracking.
- During hydrotreating, sulphur and nitrogen concentration in the final products is reduced along with the saturation of olefins and aromatics. However, boiling range of the final products will be similar to that of the feed stock.
- During hydrocracking, heavier molecules react with hydrogen to generate lighter hydrocarbons.

Process Conditions

- Depending upon the feed conditions, the operating conditions are
 - o Temperature: 290 – 430 oC
 - o Pressure: 7 – 180 bar
- Higher pressure and temperature are used when heavier feed stocks are used.
- Catalysts: Cobalt, Molybdenum catalysts are used when effective sulphur removal is targeted. Nickel, molybdenum catalysts are used when effective nitrogen removal is targeted
- The hydrotreating reactions are exothermic and therefore, the reactor product needs to be cooled.



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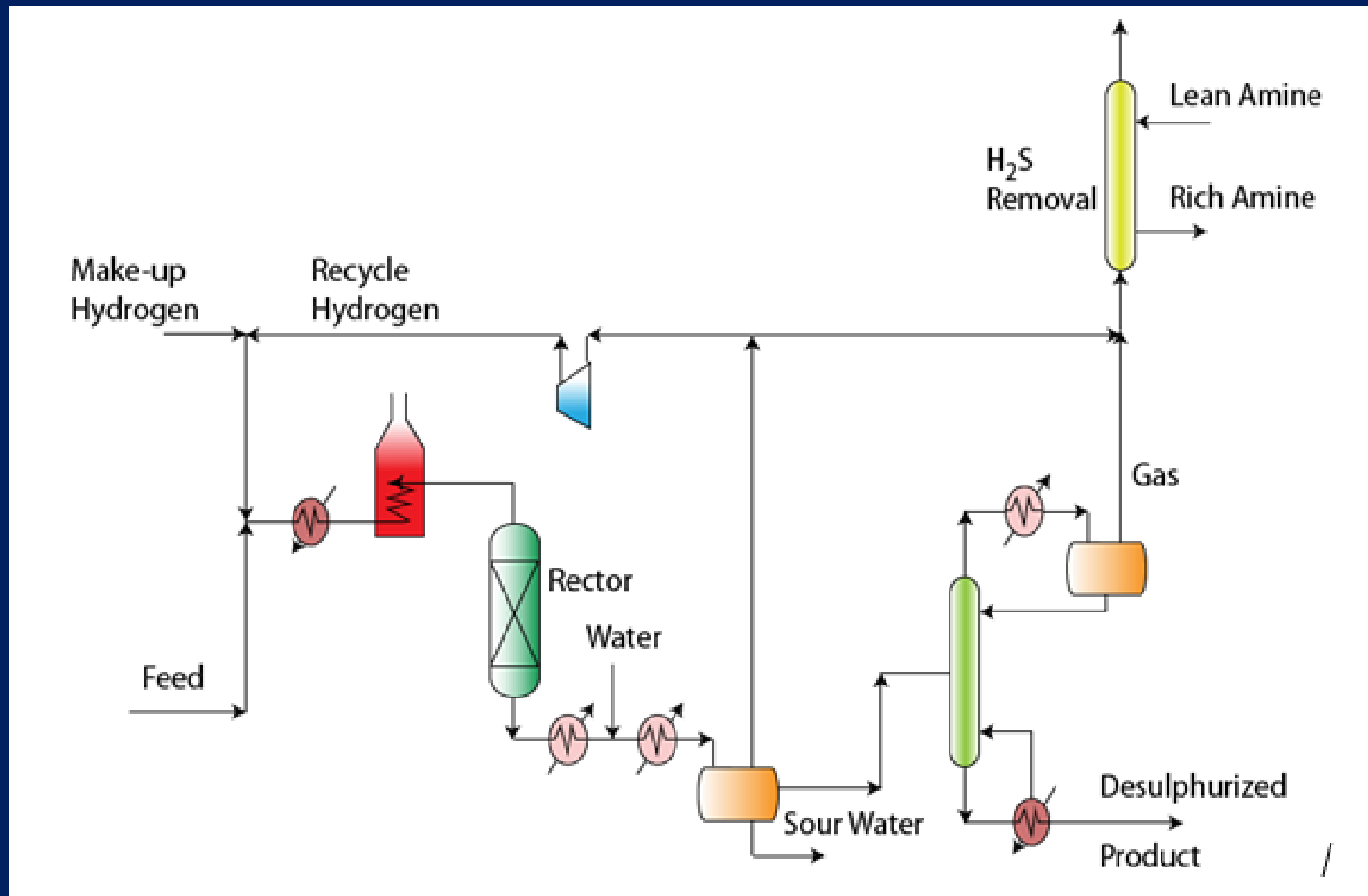
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REFINERY PROCESS-HYDRO-PRECESSING UNIT BASICS

- Feed is mixed with recycle hydrogen stream
- Sent to heat exchange in a furnace for heating the same
- Eventually the heated feed mixture is sent to the hydrotreating packed bed reactor
- The reactor outlet is cooled and mixed with water.
- Eventually the water mixed reactor stream is further cooled and sent to a phase separator.
- The phase separator splits the feed stream to three separate streams namely a gas phase stream, an organic stream and an aqueous stream.
- The aqueous stream is rich of H₂S and NH₃ and will be sent out to a sour water processing unit to recover H₂S and NH₃. The sour water processing unit uses amine based absorption technology to recover H₂S.
- The hydrotreated product is the organic stream enters a fractionator to stabilize the hydrotreated product. Eventually the stabilizing fractionator produces a gas stream from the partial condenser consisting of H₂, C₁-C₄, H₂S and NH₃.

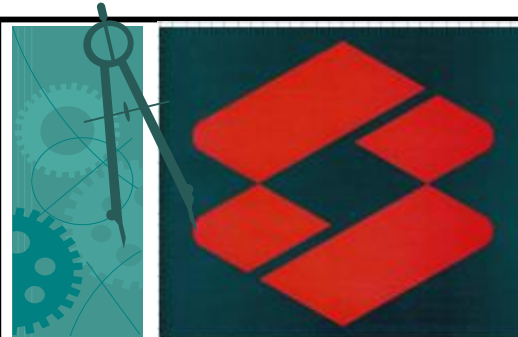


-The gas stream emanating from the phase separator consists of 60 – 90 % H₂. Majority of this stream is recycled using a compressor to mix with the make-up hydrogen and enter the heat exchanger and furnaces. The other part of the gas stream from the phase separator is purged to mix with the gas generated from the fractionators and enter the absorption unit for H₂S removal.

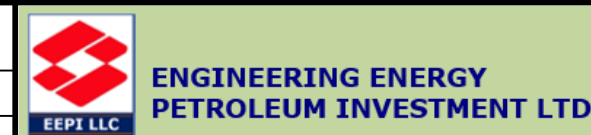
-When high sulphur feeds are used, H₂S removal is carried out by placing an additional absorber unit (with amine as an absorbent) to reduce higher concentrations of H₂S in the gas stream. In this case, a purge stream is allowed to balance off the additional gas available as another by product from the process.

Process technology for Residue hydrotreating

- Heavier hydrocarbon hydrotreating is carried out using guard reactors
- Guard reactors have catalysts with larger pore size first and then have decreasing pore size along the reactor length.
- The guard reactors are followed with conventional packed bed reactors.
- This is due to the reason that heavier fractions could form coke and damage the catalyst totally.
- Here, Nickel and Vanadium would stay back on the surface of the catalyst
- Except the guard reactors, the remaining flow sheet for residue hydrotreating remains the same. Live steam is used in the fractionator and unstabilized naphtha is produced as one of the products in the residue hydrotreating process.



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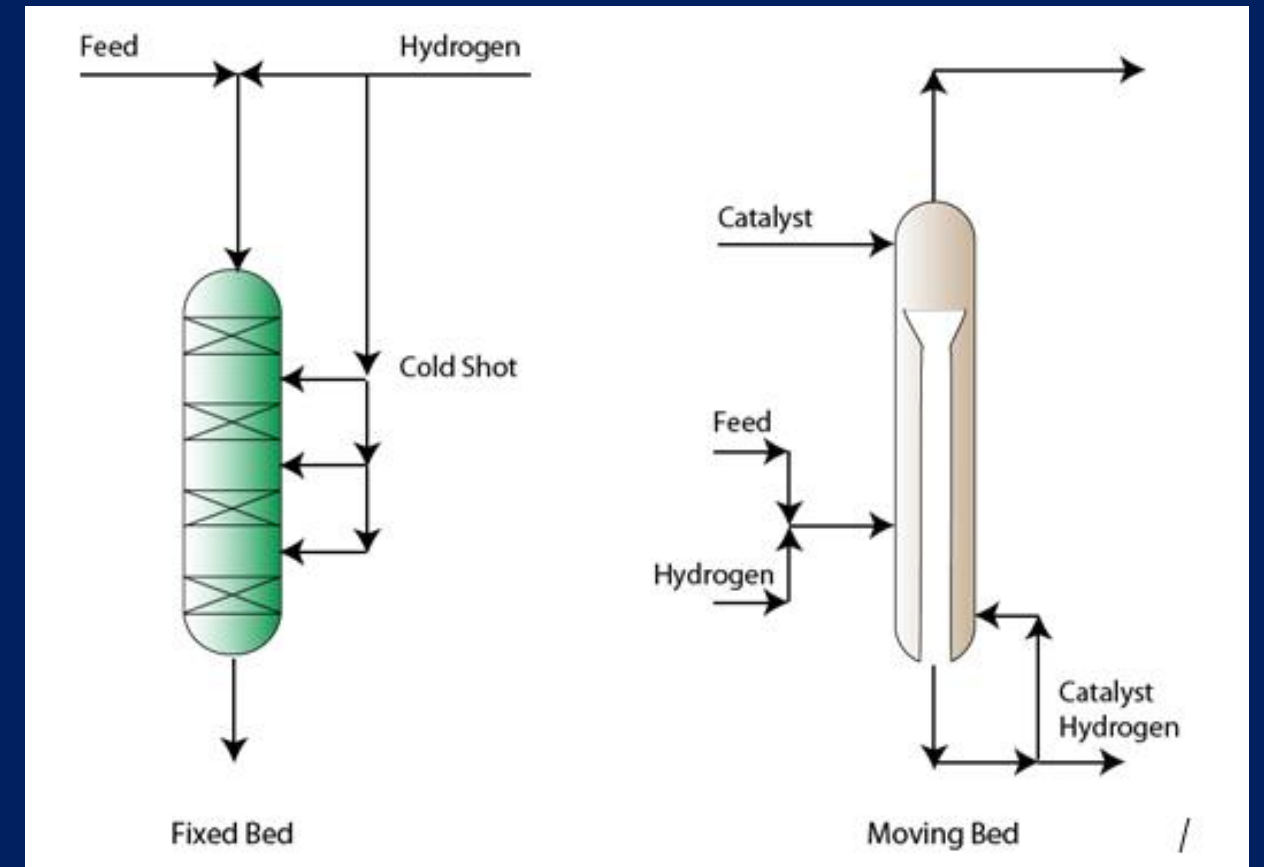


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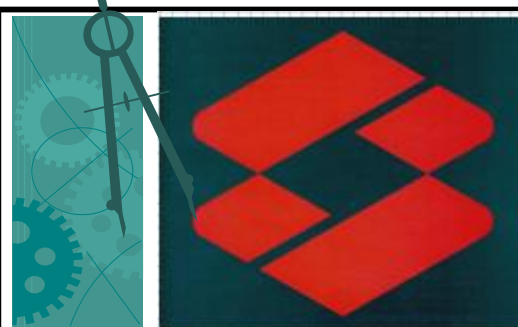
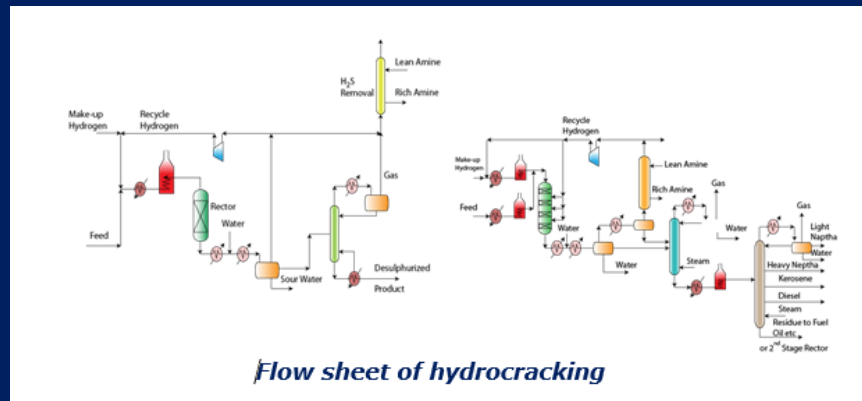
Hydrocracking

Process summary

- Cycle oils and coker distillates are the typical feedstocks
- High quality jet fuel and diesel production is targeted
- Overall reaction is exothermic
- Cracking is promoted on silica-alumina sites of the catalyst. Hydrogenation promoted by palladium, molybdenum sulphide or tungsten sulphide compounds
- Since catalyst gets poisoned with organic nitrogen compounds, hydrotreater catalytic reactors are used before hydrocracking reactors to safeguard the hydrocracking catalysts
- Excess hydrogen also aids in preventing catalyst coking.
- Operating conditions of the hydrocracking reactor: 340 – 425 oC and 70 – 200 bar



- Reactors use fixed or moving bed reactors in which fixed beds are more common.
- Packed beds: Cold shot reactors are used in which cold H₂ is used to cool the hot streams. Guard reactors are used before hydrocracking catalyst within the reactor column itself
- Moving beds: Feed allows movement of the catalyst for good mixing.
- After reaction, the product gets mixed with water and enters a three phase separator.



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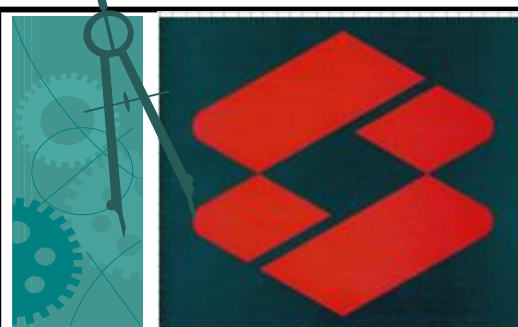
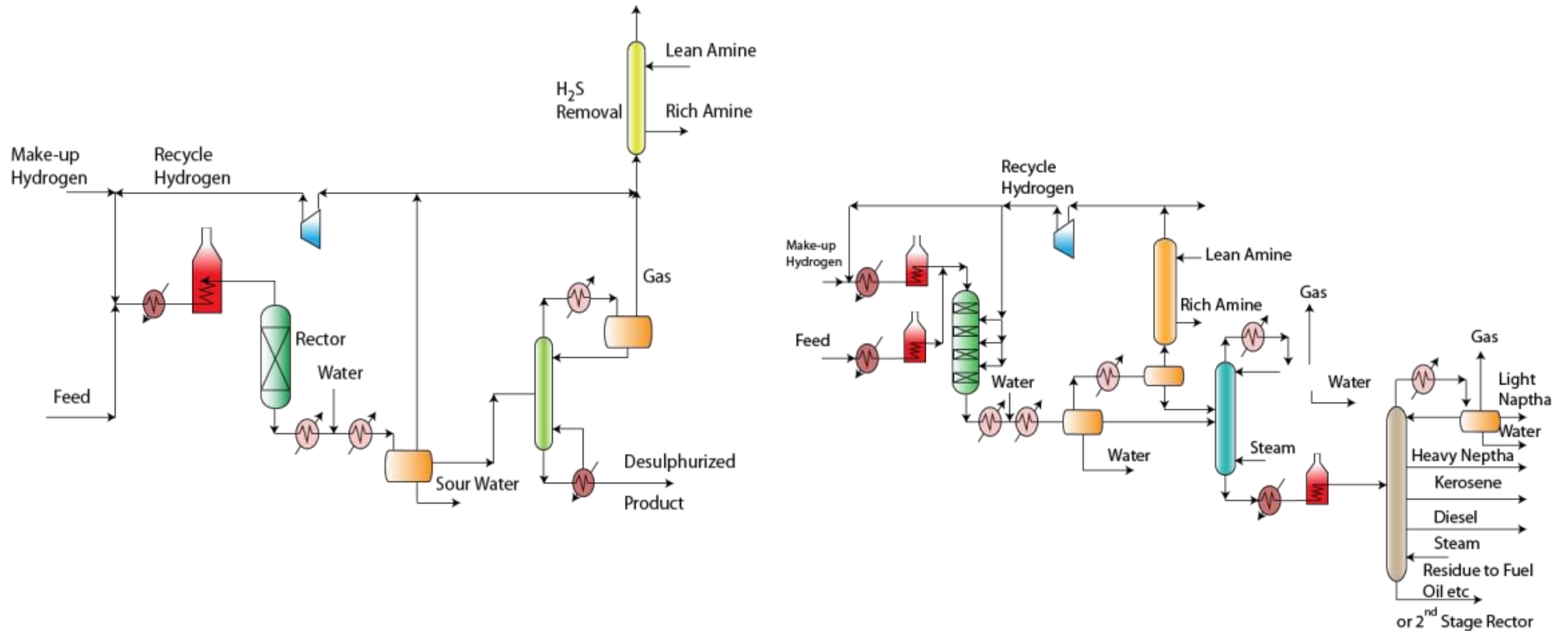
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REFINERY PROCESS-HYDRO-PRECESSING UNIT BASICS

- The three phase separator generates three streams namely sour water stream, organic stream and a gas stream.
- The gas stream again enters a phase separator to remove entrained organic stream after cooling.
- The gas stream is subjected to H₂S removal using amine scrubber. The organic stream eventually enters a steam stripper further stabilize the organic stream. In this fractionator, a gas stream and a sour water stream are generated.
- Eventually, the stabilized organic stream is sent to a multi-product fractionators to generate light naphtha, heavy naphtha, kerosene, diesel and residue. Steam is used to enhance the product quality.



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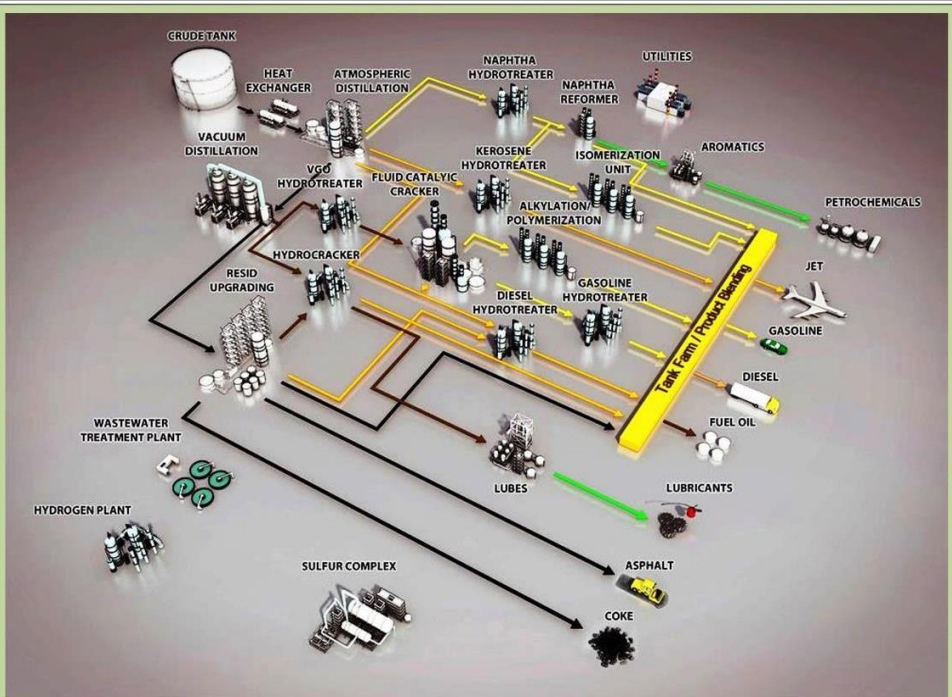
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REFINERY PROCESS-ALYKLATION-PRECESSING UNIT BASICS



22

Refinery Siting Workbook
Appendices A & B
February 2018

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ChNPZ NEFTKHM REFINERY-PROCESS UNITS DESCRIPTION

BOTTOM OF THE BARREL EPCF TURNKEY DELIVERY

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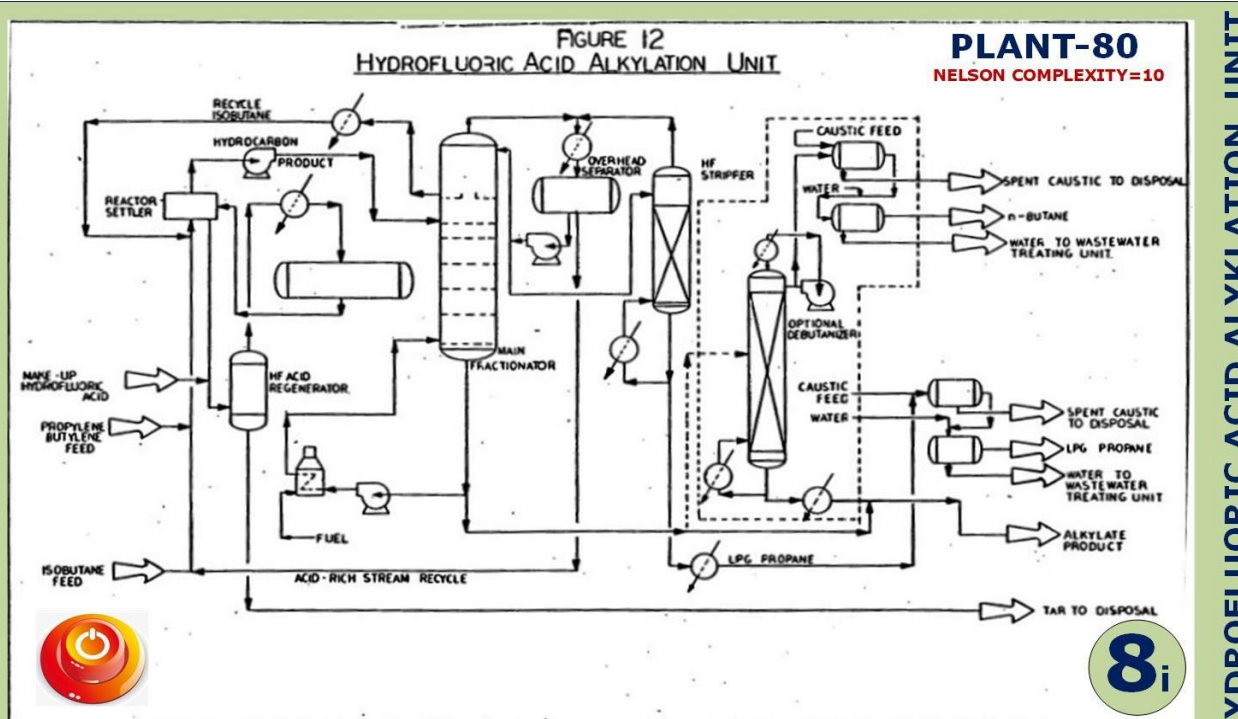


FIGURE 12 HYDROFLUORIC ACID ALKYLATION UNIT

PLANT-80 NELSON COMPLEXITY=10

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HYDROFLUORIC ACID ALKYLATION UNIT

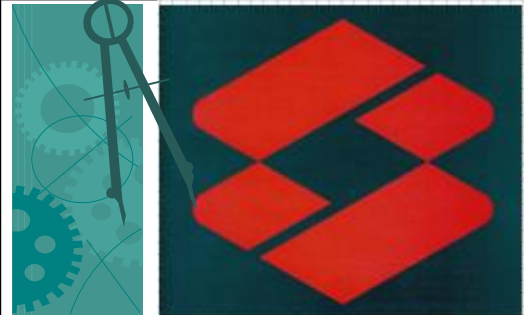
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SEE BOOK-22 PAGE-9 ALYKLATION UNIT

- In this lecture, we present a brief overview of the alkylation process.
- In an alkylation process, olefins are reacted with isoparaffins to yield alkylate product.
- The basic purpose of alkylation is to enhance the octane number of the feed stock.
- For instance, octane number of butane alkylate is about 92 - 97. This is due to the formation of a hydrocarbon with side chain arrangement of carbon and hydrogen atoms.



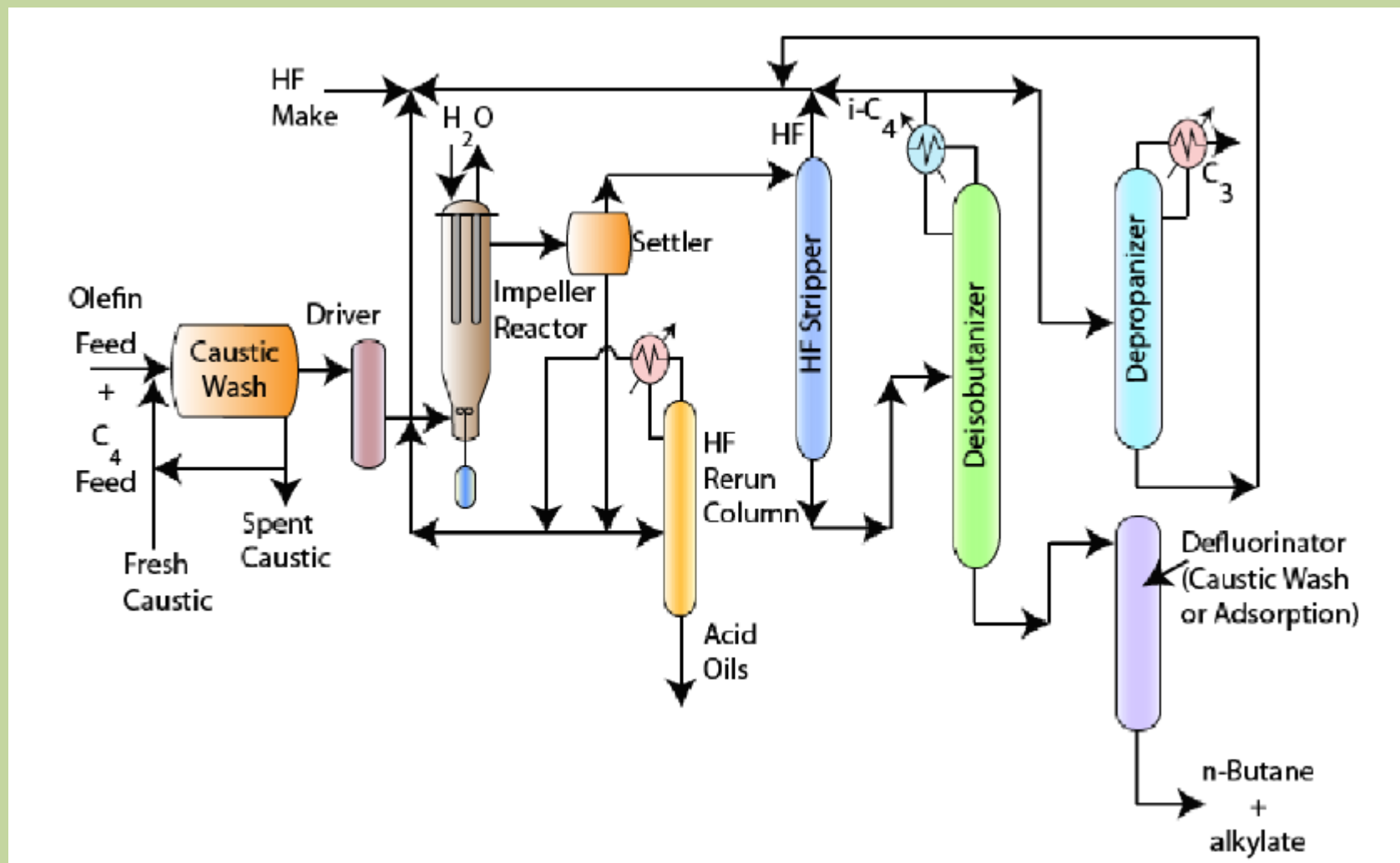
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REFINERY PROCESS-ALKYLATION-PREPROCESSING UNIT BASICS

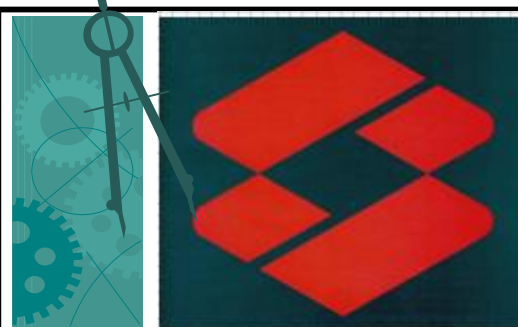
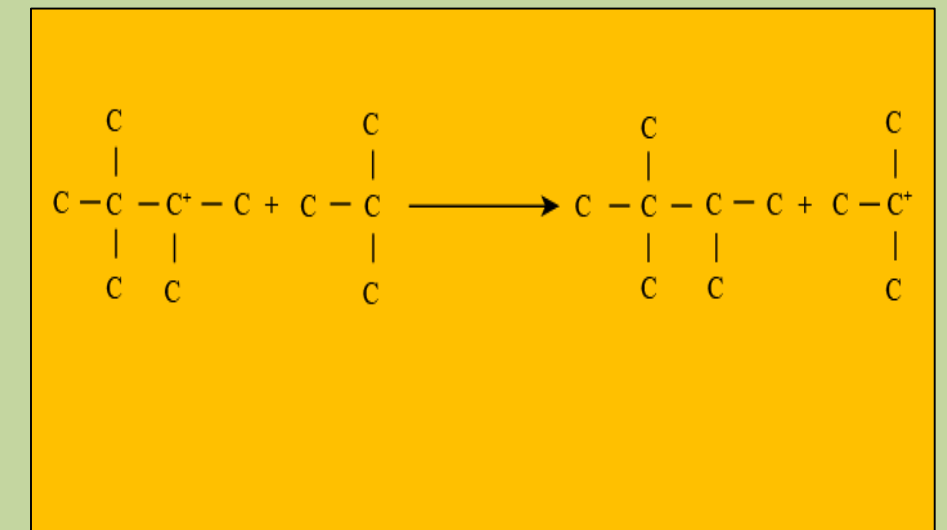
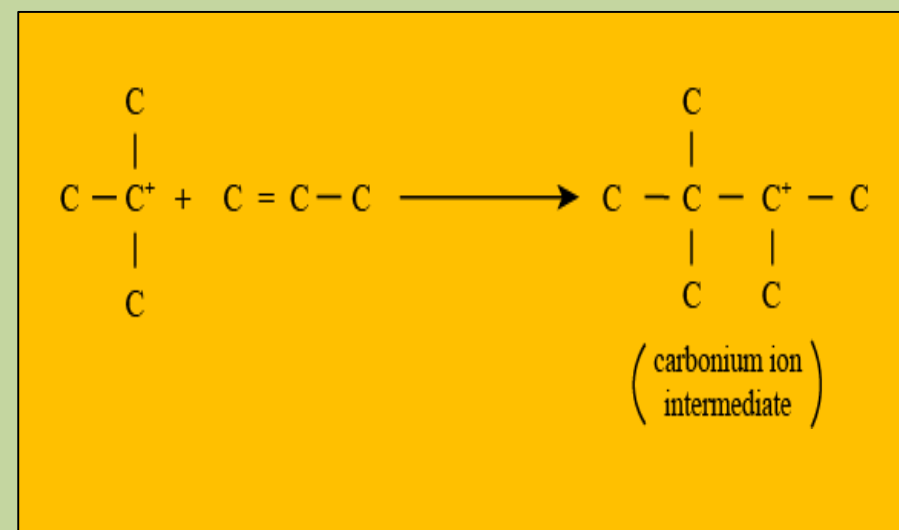
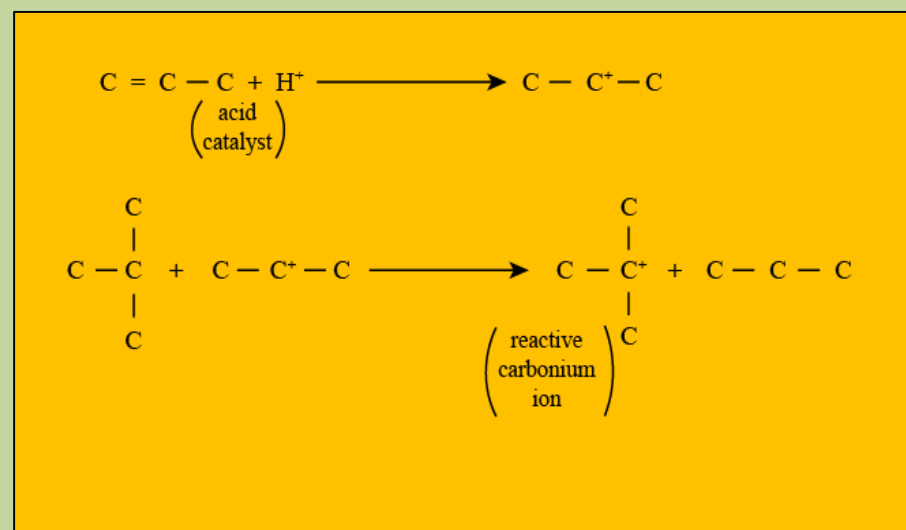


Reaction Mechanism

- There are three basic reaction steps to achieve alkylation
- **Step 1** involving Carbonium ion formation: In this reaction, alkene reacts with a proton (acid catalyst) to produce a proton substituted olefin. The proton substituted olefin reacts with isoparaffin to generate a reactive carbonium ion and alkane.
- **Step 2** involving carbonium ion intermediate formation: In this reaction, the carbonium ion formed in step 1 reacts with the olefin to produce an intermediate carbonium ion.
- **Step 3** involving regeneration of carbonium ion: In this reaction, the intermediate carbonium ion reacts with the isoparaffin to produce alkylate product and carbonium ion. Thus carbonium ion is again regenerated to take part in step 2 reactions along with other additional unreacted olefin molecules.

Reaction conditions

- To avoid olefin polymerization, high isobutane to olefin ratios are used.
- Typical isobutene to olefin ratios are 5:1 to 15:1
- Acid catalysts are used. Primarily sulphuric acid (H₂SO₄) or HF are used.
- Depending on the acid catalysts chosen the process complexity varies. We present both process technologies to indicate the pertinent process complexity.
- Reaction operating temperature: 10 - 20 oC using H₂SO₄ and 25 - 40 oC using HF



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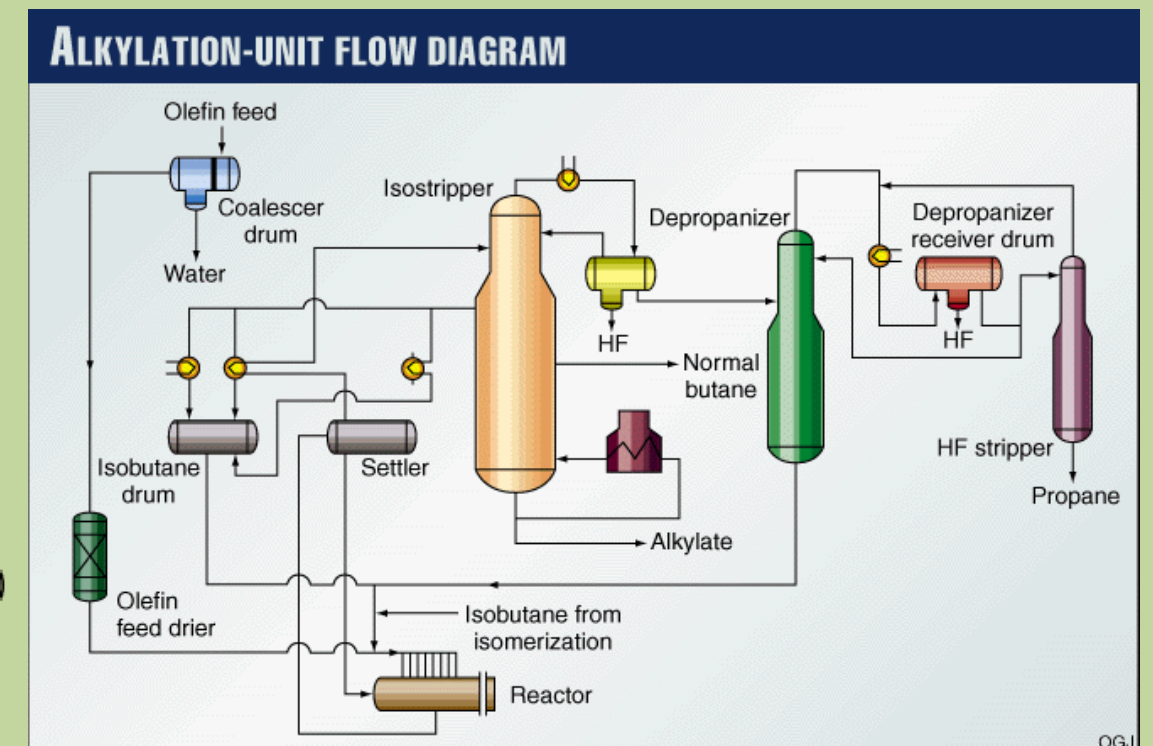
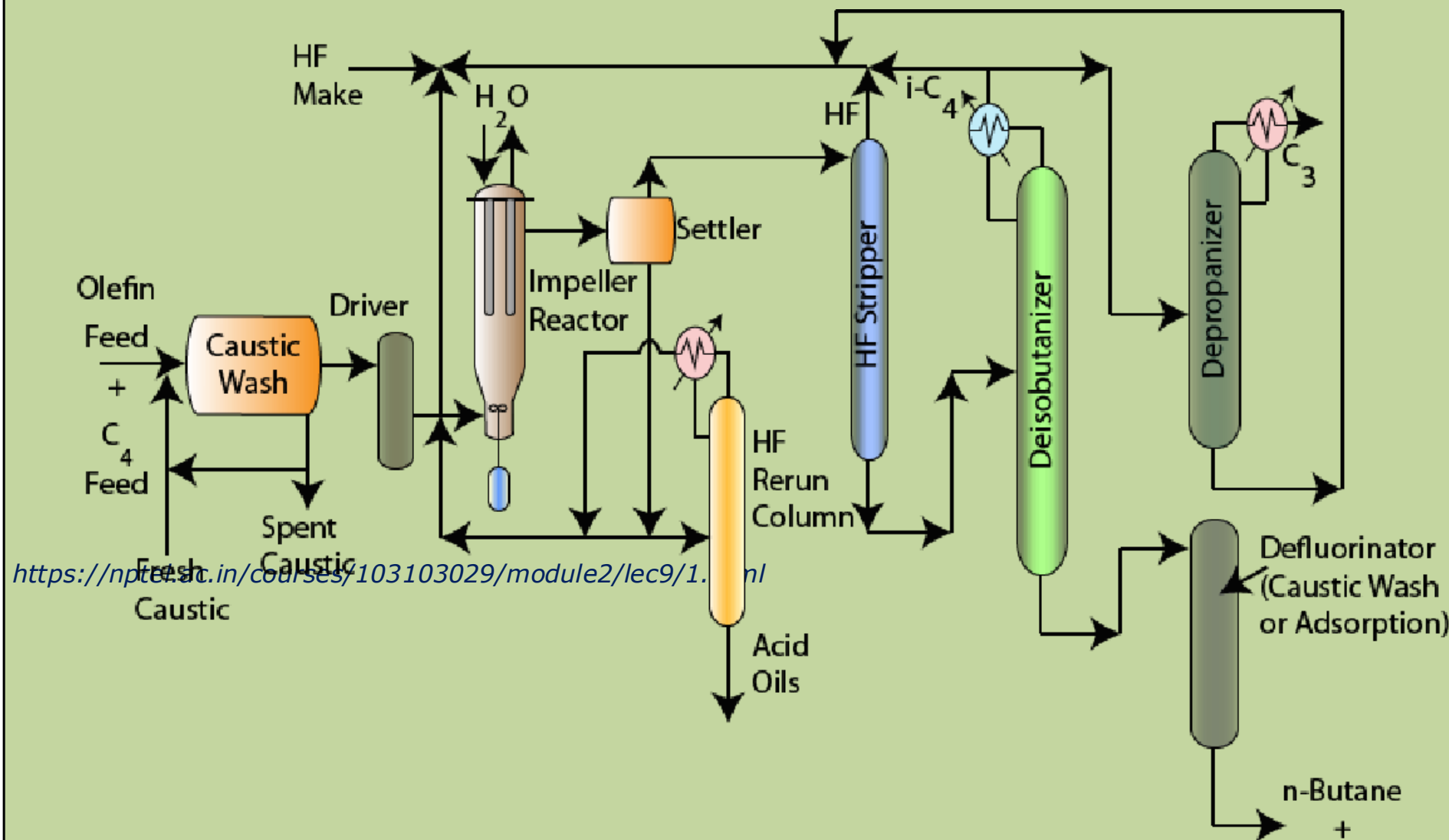
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REFINERY PROCESS-ALYKLATION-PRECESSING UNIT BASICS

HF process technology

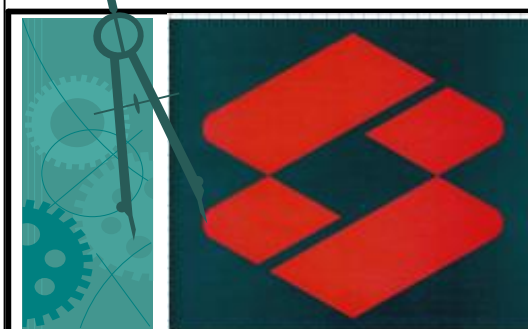
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<https://nptel.ac.in/courses/103103029/module2/lec9/1.html>

- The process is similar to the sulphuric acid plant. However, additional safety issues make the process complex.
- The feed is first subjected to drying followed by pre-cooling.
- After pre-cooling the reaction mixture, the reaction mixture is fed to a reactor.
- Unlike CSTRs in series here impeller reactors are used. The reactor consists of cooling tubes to absorb the heat generated.
- The reaction products enters a settler where oil and the HF are separated.
- Since there can be traces of HF in the oil rich phase and vice-versa additional processing is followed.
- The HF rerun column removes traces of oils from the bulk of the HF. Thus HF purified will be recycled back to the reactor. The bottom product thus generated in this unit is acid oils.
- A HF stripper is used to remove the HF in lower quantities from the alkylate product. Eventually, the HF stripper produces HF that is sent back to the reactor and the alkylate product.
- The alkylate product is sent to a deisobutanizer and depropanizer units. The final alkylate product is produced by using a defluorinator which is basically a caustic wash or adsorption unit. Finally n-butane + alkylate is produced as the bottom product.



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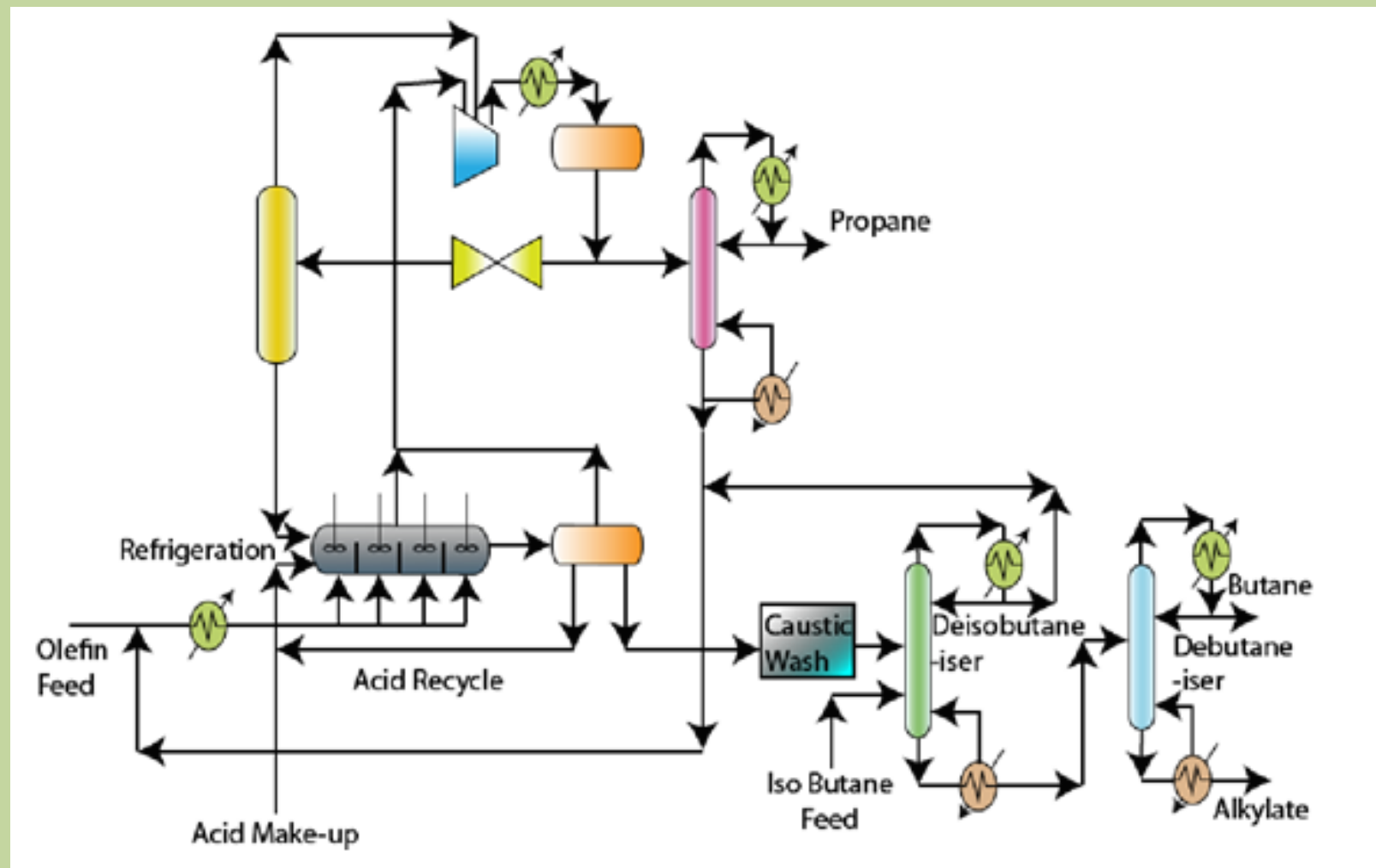
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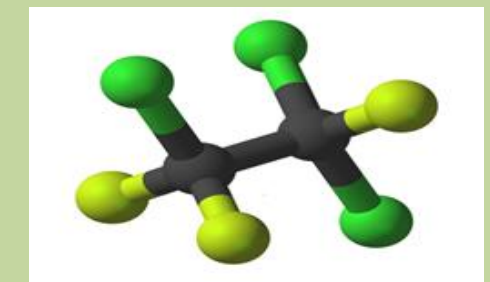
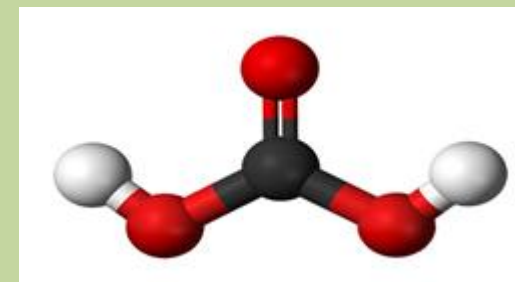
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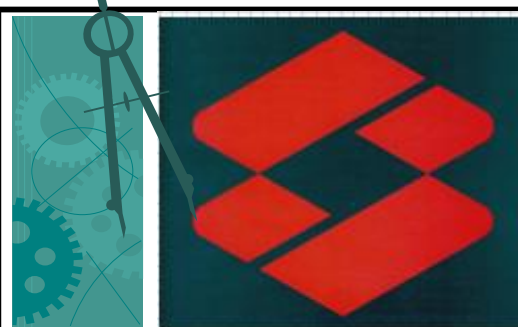
REFINERY PROCESS-ALKYLATION-PREPROCESSING UNIT BASICS



- **Caustic wash:** The feed mixture (olefin + C4 compounds) are first subjected to caustic wash. During caustic wash, sulphur compounds are removed and spent caustic is recycled back to the caustic wash. Fresh caustic solution is added to take care of the loss.
- **Refrigeration:** The olefin feed enters a refrigeration unit to reduce the feedstock temperature.
- **Alkylation reactor:** The reactor is arranged as a series of CSTRs with acid fed in the first CSTR and feed supplied to different CSTRs. This arrangement is for maximizing the conversion.
- In the alkylation reactor it is important to note that the olefin is the limiting reactant and isoparaffin is the excess reactant.
- The alkylator unit therefore will have two phases in due course of reaction namely the olefin + isoparaffin mixture which will be lighter and the alkylate stream which will be heavier and will be appearing as a bottom fraction if allowed to settle.
- Since excess isoparaffin is used, the isoparaffin can be easily allowed as a bypass stream.



- Eventually, the alkylate product from the last reactor will be taken out as a heavy stream.
- Thus, the alkylation reactor produces two streams. These are (a) isoparaffin rich organic phase and (b) alkylate rich phase along with acid and isobutane phases.
- These streams should be subjected to further purification.
- **Phase separator:** It so happens that the acid enters the organic rich stream and will be subjected to phase separation by settling. Similarly, the olefin/isoparaffin mixture will be also separated by gravity settling. Thus the phase separator produces three streams namely (a) olefin + isoparaffin rich phase (b) acid rich stream (c) alkylate rich stream.
- **Olefin + Paraffin processing:** The olefin + paraffin stream is first subjected to compression followed by cooling. When this stream is subjected to throttling and phase separation, then the olefin + paraffin rich stream will be generated. The propane rich stream from this stream is generated as another stream in the phase separator.
- **Propane defractionator:** The propane rich stream after cooling is fed to a fractionator where propane is separated from the olefin+isoparaffin mixture. The olefin+isoparaffin mixture is sent back to mix with the olefin feed.
- **Caustic wash for alkylate rich stream:** The caustic wash operation ensures to completely eliminate acid concentration from the alkylate.
- **Alkylate fractionation:** The alkylate is fed to a distillation column that is supplied with isobutane feed and alkylate feeds to produce isobutane as a top product and alkylate + butane mixture as a bottom product.
- **Debutanizer:** The debutanizer separates butane and alkylate using the concept of distillation



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REFINERY PROCESS-VISBREAKING AND COKING-PREPROCESSING UNIT BASICS

- In this lecture, we present two important processes that are used to upgrade the residue product obtained from the vacuum distillation unit.
- Significant amounts of vacuum residue is obtained from various crude oils. For instance Arabian heavy oil produces 23.2 vol% vacuum residue product.
- The residue consists of heavier hydrocarbons with molecular weights ranging from 5000 – 10000.
- Thermal cracking is most preferable for the vacuum residue.
- The vacuum residue also consists of other metals such as vanadium and nickel.
- Typically, vacuum residue is subjected to six different operations namely
 - o Vacuum residue desulphurization (VRDS)
 - o Residue fluid catalytic cracking (RFCC)
 - o Visbreaking
 - o Coking
 - o Deasphalting
 - o Gasification
- Amongst these, Visbreaking and coking are prominent operations that exist in many refineries and we restrict our discussion to these processes only.

Visbreaking

- In Visbreaking operation, a mild thermal cracking is carried out.
- Visbreaking produces **Naphtha, Gasoil and a residue**. The residue has lower viscosity and pour point and hence can easily meet the requirements of the fuel oil specifications in the fuel oil blending pool.
- Visbreaking basically breaks the long paraffinic side chains attached to aromatic structures. Due to this the residue pour point and viscosities are considerably reduced.
- Two classes of reactions occur during visbreaking
 - o Cracking of side chained aromatic compounds to produce short chained aromatics and paraffins
 - o Cracking of large molecules to form light hydrocarbons

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CHNPZ NEFTKHM REFINERY-PROCESS UNITS DESCRIPTION

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https://en.wikipedia.org/wiki/Delayed_coker

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FIGURE II DELAYED COKING UNIT

PLANT-70 NELSON COMPLEXITY=6

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REFINERY DESIGN BASICS

CONCEPTUAL DESIGN PRESENTATION

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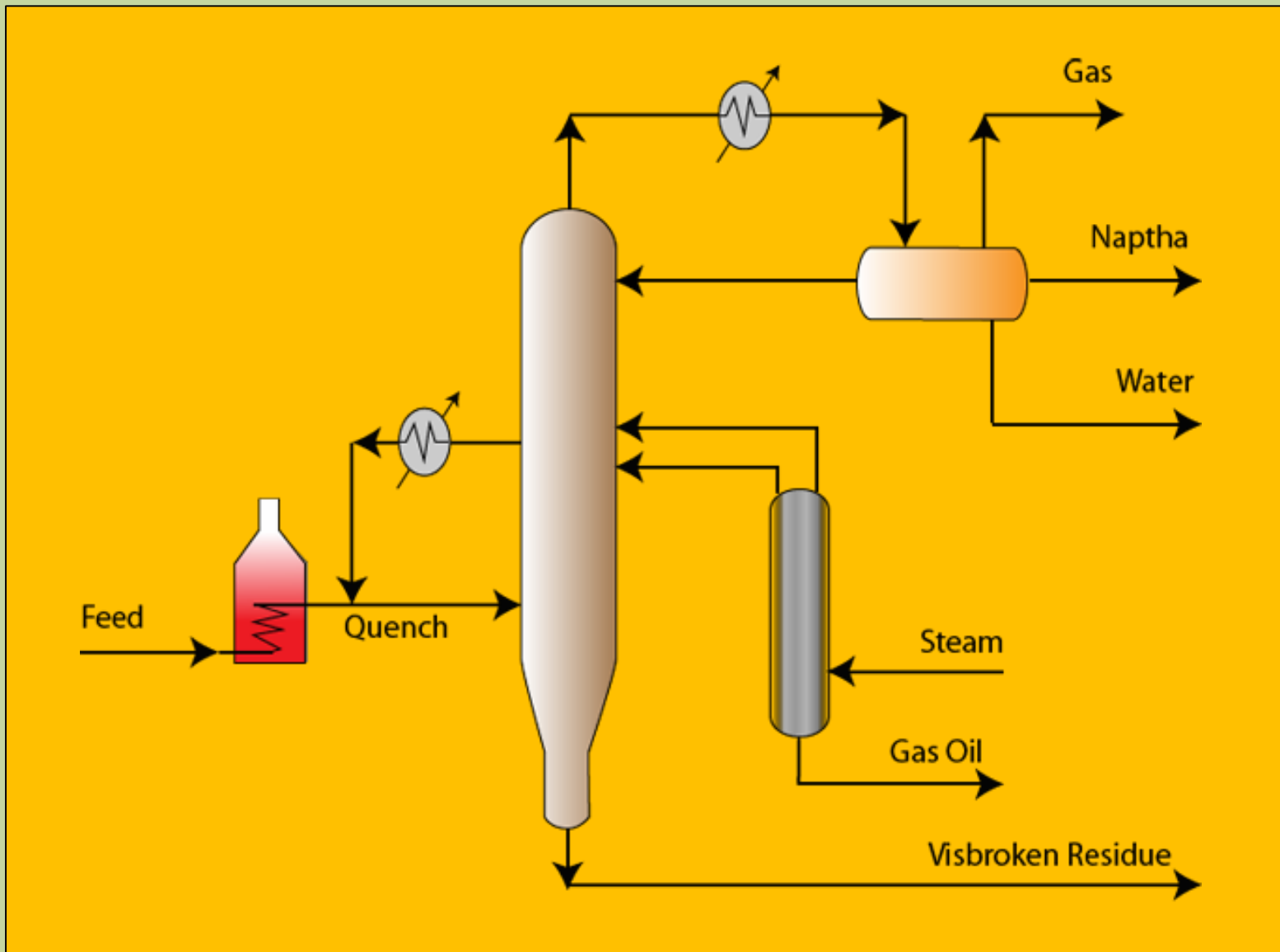
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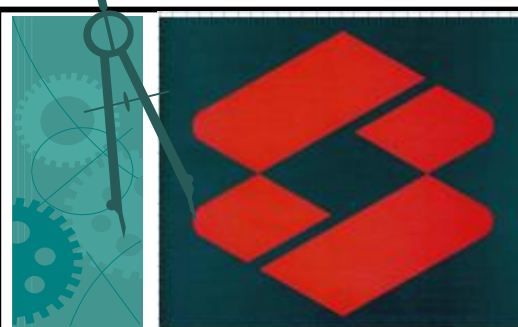
REFINERY PROCESS-VISBREAKING AND COKING-PRECESSING UNIT BASICS

- Visbreaking is carried out either in a coil or in a soaker.
- When coil technology is used, the mild thermal cracking is carried out in the furnace coils
- When soaker technology is adopted, the cracking is carried out in a soaker unit that is kept immediately after the furnace.
- After cracking, the products are at high temperatures (480 °C for coiled furnace case or 430 °C for the soaker)
- After cracking, the products are cooled using quenching operation.
- Quenching is a direct heat transfer mechanism in which a hot stream is cooled with a hydrocarbon or water to reduce the temperature of the system drastically.
- After quenching, the mixture is fed to a distillation column supplemented with a side column and a partial condenser
- From partial condenser, water, naphtha and gas are produced. Naphtha liquid stream is sent as a reflux for the column.
- The side column is fed with steam and produces gas oil. Steam enhances hydrocarbon volatility as explained before in the lecture devoted towards crude distillation process.



Coil Visbreaking vs Soaker Visbreaking

Coil Visbreaking (Low Residence time Cracking)	Soaker Visbreaking (high residence time cracking)
<ul style="list-style-type: none"> • Coil visbreaking is applied to the cracking process units where cracking process occur in a furnace tube. 	<ul style="list-style-type: none"> • In this bulk cracking reaction occur not in the furnace but in a drum located after the furnace.
<ul style="list-style-type: none"> • The higher temperatures are used in coil visbreaking. 	<ul style="list-style-type: none"> • the lower temperatures are used in Soaker visbreaking.
<ul style="list-style-type: none"> • .De-coking: In this petroleum coke deposits in the tube of the furnace and leads to fouling or blocking of the tubes. 	<ul style="list-style-type: none"> • The same will occur in the drum of a soaker visbreaker, though the lower temperatures used in the soaker drum leads to fouling at a much slower rate.



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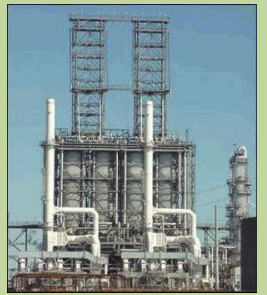
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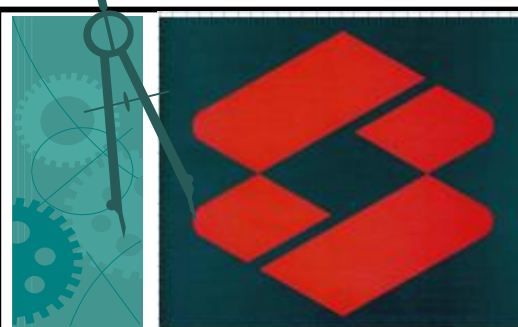
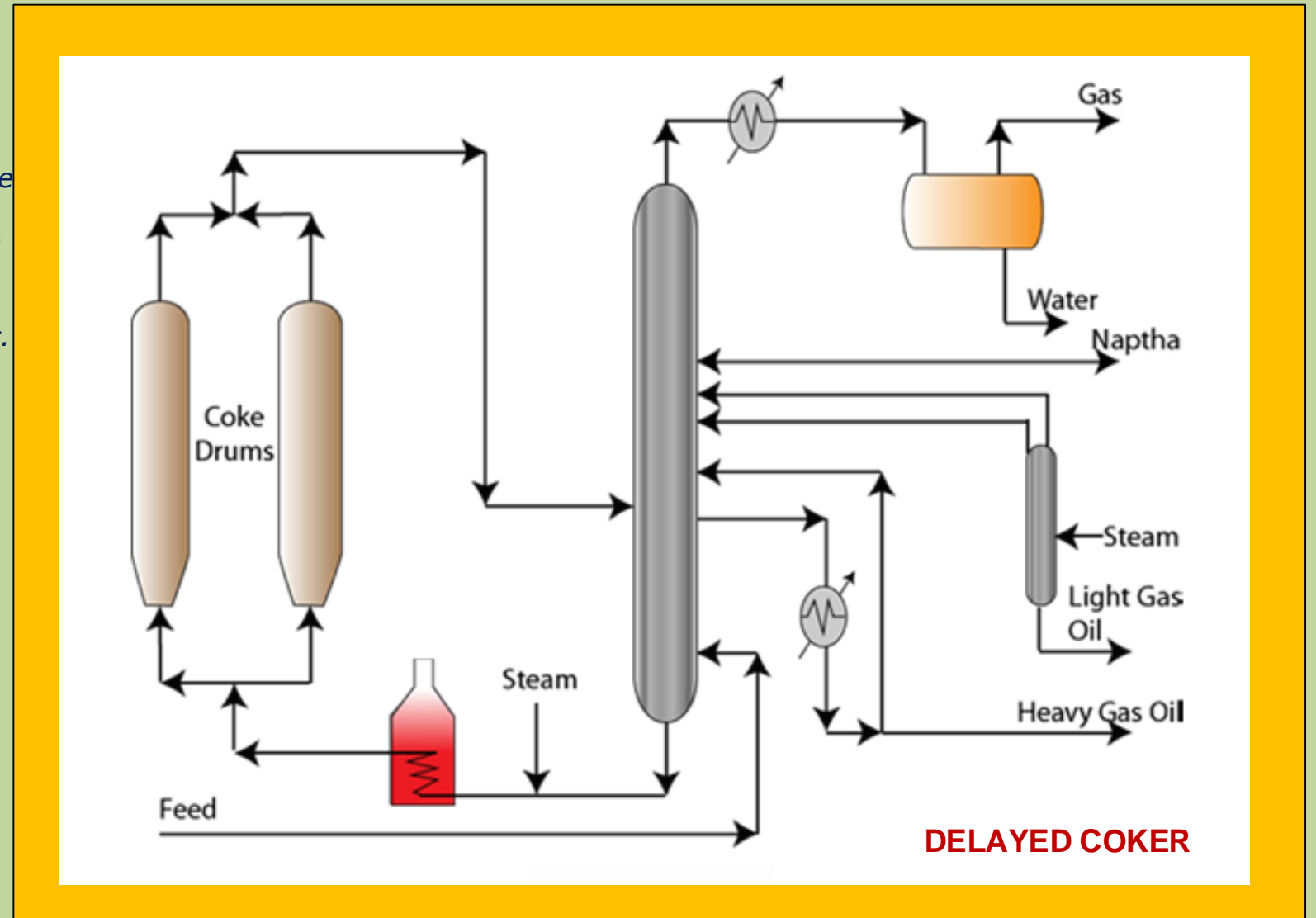
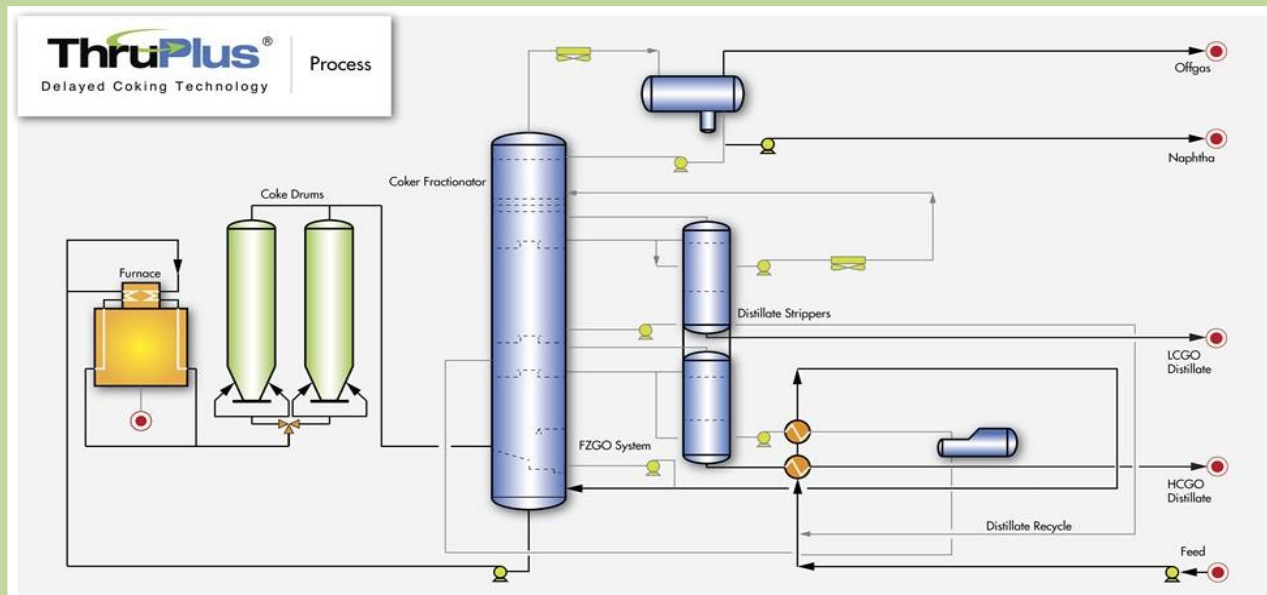
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REFINERY PROCESS-VISBREAKING AND COKING-PREPROCESSING UNIT BASICS



Coking

- Coking refers to extreme thermal cracking process
- Coking is a batch reaction. Feed is heated to 480 – 510 oC and left for some time so that coke and lighter products form.
- Since coking is a batch reaction, there can be different ways to carry out coking.
- There are two types of refinery coking processes namely delayed coking and fluid coking.
- Delayed coking: The heated feed is fed to a coke drum and coke forms in the drum. The lighter products are withdrawn from the top section of the delayed coker. After coking, the coke drum is full of coke and it is then removed using water jets. The process is called delayed coking because in this process the coal is heated using a much more complex system, and it consists of multiple furnaces or coke drums. Usually the coal is heated at a lower temperature for shorter periods of time, which removes water and other by-products more slowly than the conventional process, thereby increasing the overall time span.
- Fluid coking: The heated feed is fed to a fluidized bed where coke particles with finer particle sizes would aid fluidization. After coking, lighter products are withdrawn as overhead vapour and coke thus formed is removed continuously. The fluid coker also has an additional scrubber which will remove heavier compounds from the vapors (if any) and send them back with the feed stream. Here, the feed stream absorbs heavier hydrocarbons from the vapors generated. This is required as it is difficult to keep heavier hydrocarbons in the feed phase only due to pertinent high temperatures. The coke after coking reaction is cold coke. Therefore, to generate hot coke, a burner unit is used to heat the coke using exothermic CO₂ reaction. The offgases from the burner are sent to cyclones, scrubbing and then to the vent. The hot coke thus obtained is recycled back to the fluidized bed or taken out as a net coke product.



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REFINERY PROCESS-VISBREAKING AND COKING-PREPROCESSING UNIT BASICS

Fluid coking:

The heated feed is fed to a fluidized bed where coke particles with finer particle sizes would aid fluidization. After coking, lighter products are withdrawn as overhead vapour and coke thus formed is removed continuously. The fluid coker also has an additional scrubber which will remove heavier compounds from the vapors (if any) and send them back with the feed stream. Here, the feed stream absorbs heavier hydrocarbons from the vapors generated. This is required as it is difficult to keep heavier hydrocarbons in the feed phase only due to pertinent high temperatures. The coke after coking reaction is cold coke. Therefore, to generate hot coke, a burner unit is used to heat the coke using exothermic CO₂ reaction. The offgases from the burner are sent to cyclones, scrubbing and then to the vent. The hot coke thus obtained is recycled back to the fluidized bed or taken out as a net coke product.

- The coker products are fed to a complex distillation column i.e., main column supplemented with side columns. From the complex distillation column, naphtha, water, light gas oil and heavy gas oil are obtained.
- Additional complexities in the distillation unit are Feed entering the distillation column but not the coker unit: This is to facilitate the removal of light ends from the feed (if any) and don't subject them to cracking. This is also due to the reason that light ends are valuable commodities and we don't want to lose them to produce cheap coke product. In this case, the bottom product from the distillation column is fed to the furnace for pre-heating and subsequent coking operation.

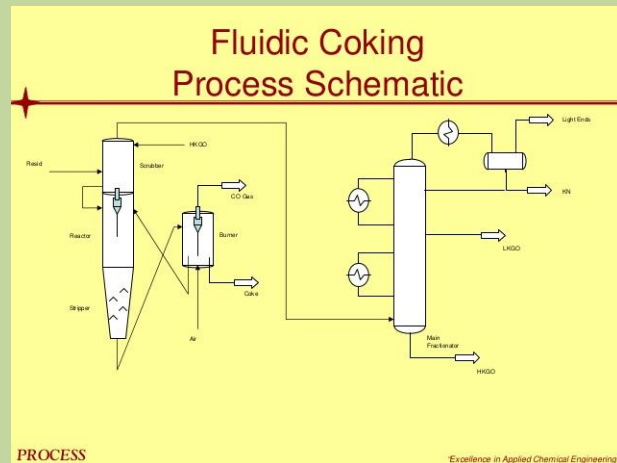
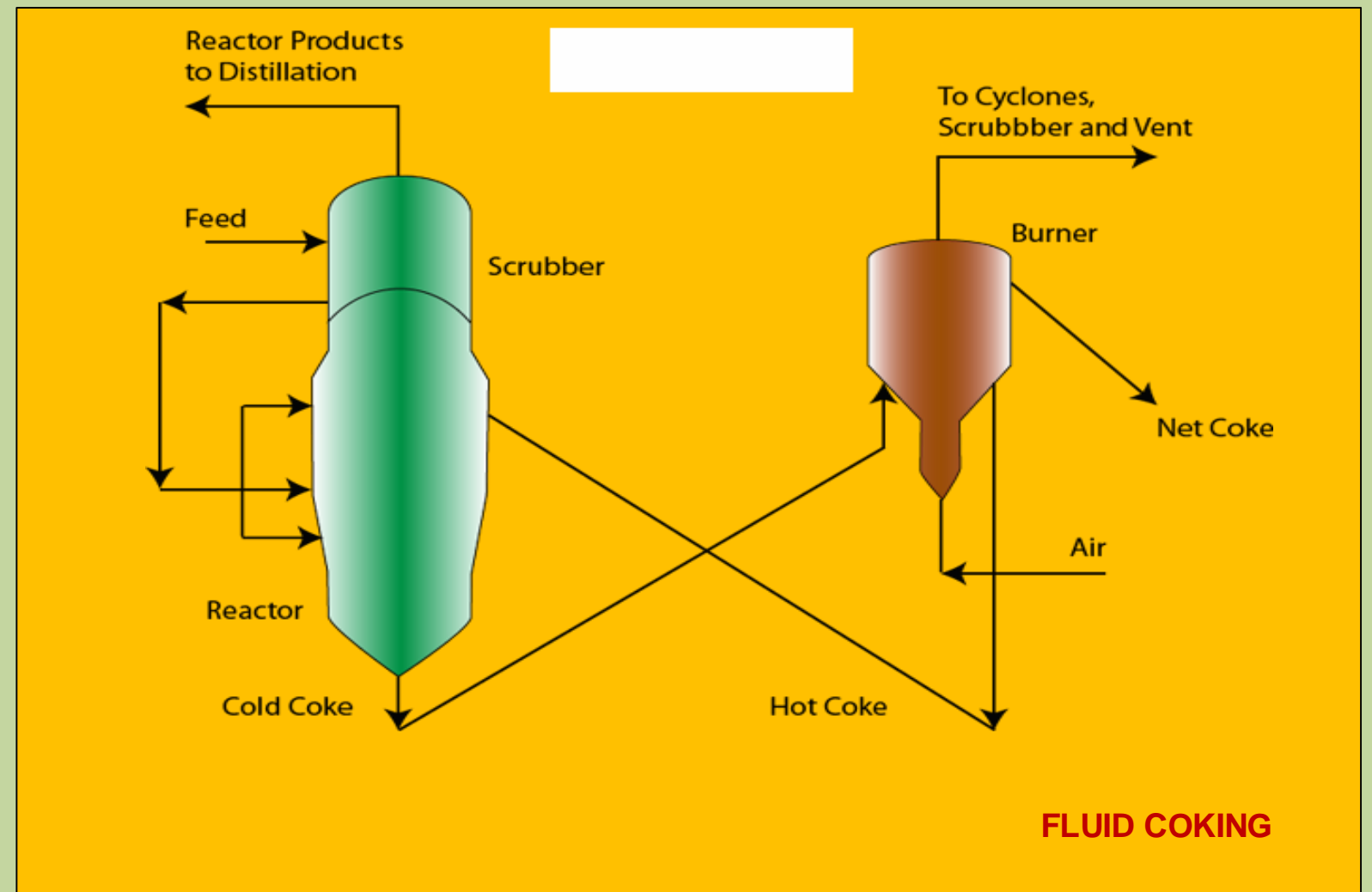
- o Live steam in distillation: This is to facilitate easy removal of lighter hydrocarbons in various sections.
- o Circulatory reflux (Pump around units): This is to facilitate good amount of liquid reflux in various sections of the main column. For Further details, of the above two issues, please refer to the crude distillation lecture notes.

What is flexicoking?

Ans: In flexi coking, coke is fed to a gasifier to react with air and steam. Eventually, the coke produces hydrogen, CO, CO₂, N₂, H₂O and H₂S. The gas thus obtained is used as a fuel gas in the refinery itself for various furnace operations. Therefore, flexicoking refers to flexibly alter the coking process to produce additionally gas using an extra gasification unit.

Flow sheets to Dekaji

1. Coil visbreaker
2. Fluid coking process Delayed coker



Delayed & Fluid Coking Processes

- Typical Yields and Dispositions

PRODUCT	Yield, wt% of feed	Disposition
Light Ends	12.5 – 20	LPG
Naphtha	10 – 15	Naphtha Hydrotreating
Light Coker Gas Oil	18 – 24	Distillate Hydrotreating
Heavy Coker Gas Oil	30 – 40	Fluid Catalytic Cracking
Pet. Coke	20 - 35	Sponge – carbon anodes; Needle – graphite electrodes; Any coke – power generation

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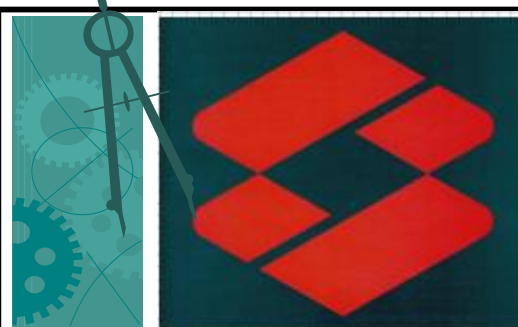
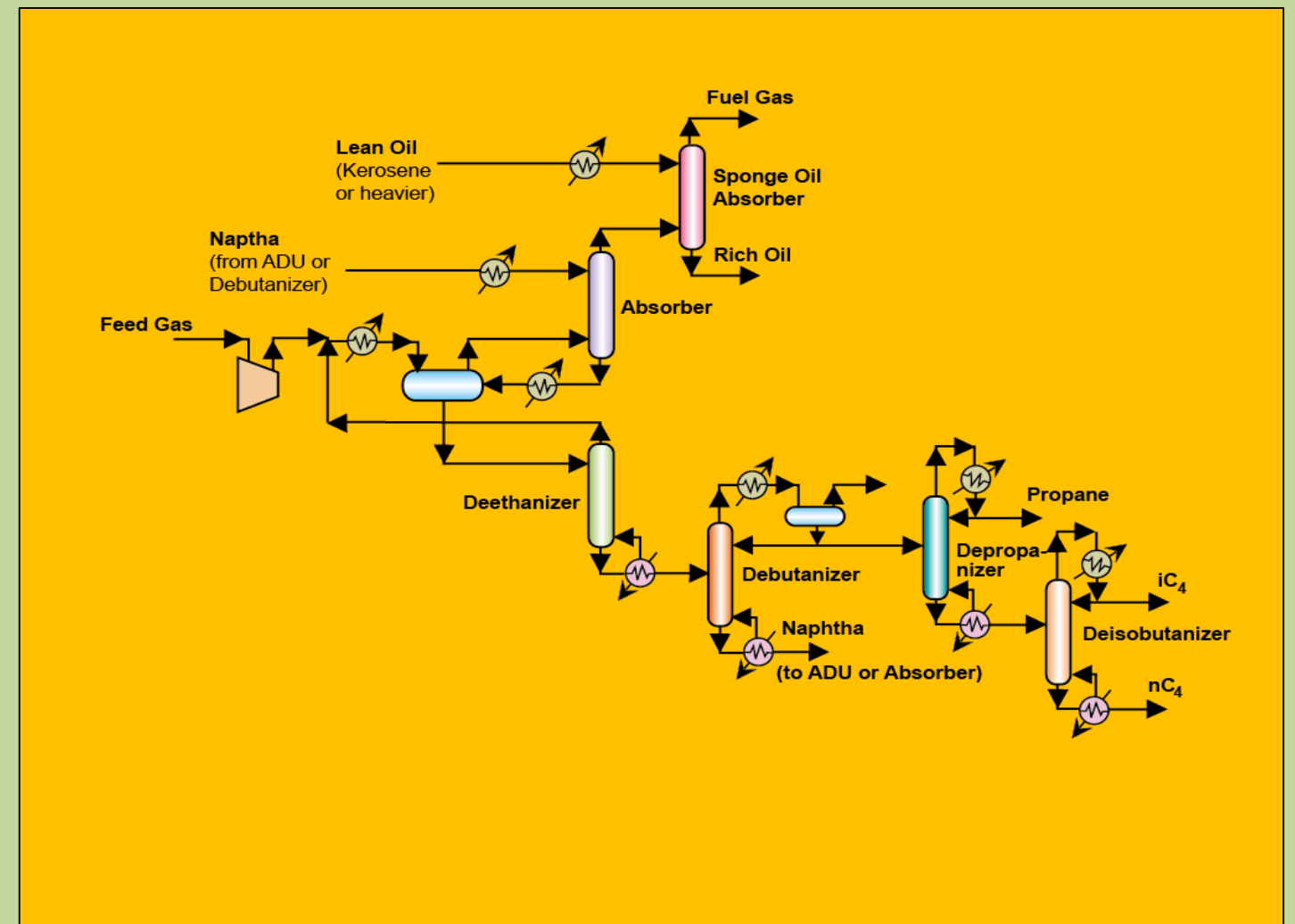
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REFINERY PROCESS-GAS PROCESSING AND POLYMERIZATION BASICS

Introduction

- In this lecture, we present an overview of light end processing followed with gas processing and polymerization processes in the refinery
- Gas fraction is produced from various units. Some of them are
 - o Crude distillation unit
 - o Catalytic cracking unit
 - o Catalytic reforming unit
 - o Hydrocracking unit
 - o Coking unit
- The light end streams are classified as
 - o Streams rich in Butane: Sold as calor gas or LPG. Used internally for blending and alkylation units (isobutane only)
 - o Streams rich in Propane
 - o Light ends rich in olefins.
- We have already studied alkylation and isomerisation as important gas processing operations. Now we will study the additional units namely gas processing and polymerization units.
- The objective of gas processing is to produce ethane and methane.
- The produced ethane and methane is to serve later for fuel gas or hydrogen production
- The gas processing section consists mainly of two different sections
- Absorption using Naphtha and kerosene:
 - o First, collected gases are compressed to be fed to an absorption.
 - o The purpose of naphtha is to absorb heavier hydrocarbons in the gas fraction. These are C3s and C4s in the feed stream. To carry out absorption, first the gases are cooled and fed to a phase separator to facilitate early separation of lighter and heavier fractions.
 - o From the phase separator two streams emanate namely a gas stream and a liquid stream.
 - o The gas stream is fed to an absorber unit where naphtha is used as a solvent to absorb the left heavier hydrocarbons in the gas.
 - o The naphtha rich with hydrocarbons is fed to the phase separator so as to stabilize the naphtha stream.
 - o The gas from the absorber is fed to a second absorber where lean oil (such as kerosene) is used as a solvent to absorb any heavier hydrocarbons other than the methane and hydrogen. Eventually, fuel gas is produced as the gas product from this absorption. The other product from the absorber is the rich oil stream
- Naphtha rich stream processing:
 - o The liquid product from the phase separator is fed to a deethanizer which generates ethane rich stream as the top product. This stream is recycled back to the gas processing unit i.e., mixing with the feed and subjected to cooling followed by phase separator.
 - o The bottom product from deethanizer is naphtha rich stream with butanes and propanes.
 - o This stream is subjected to fractionation using debutanizer, depropanizer and deisobutanizer to obtain propane, isobutane and naphtha. The stabilized naphtha can be used for absorption purposes.



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REFINERY GREEN FIELD CONFIGURATION

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REFINERY PROCESS-GAS PROCESSING AND POLYMERIZATION BASICS

Olefin Polymerization

- Olefin polymerization to yield polymer gasoline is primarily carried out to obtain polymers with good octane numbers.
- The octane number of the polymer gasoline product is not greater than the octane number of the products produced from reforming and alkylation. Instead, comparatively poor quality product is obtained. But for the sake of enhancing octane number polymerization is carried out.
-
- On the other hand, polymer gasoline has more vapour pressure than the corresponding alkylation products. Therefore, in both ways, polymer gasoline product quality is lower than that obtained from the alkylation unit.
- Typical feedstocks for polymerization process are C3 and C4 olefins that are obtained from catalytic cracking
- The end product from polymerization reactor is a dimer or a trimer of the olefins.

Reaction mechanism & Operating conditions

Reaction mechanism comprises of four basic steps

- Carbonium ion formation (Step 1): Here, olefin reacts with acid catalyst to yield carbonium ion.
- Addition reaction (Step 2): Carbonium ion reacts with olefin to generate intermediate carbonium ion
- Regeneration (Step 3): The intermediate carbonium ion converts to the dimer and generates back the proton on the catalyst surface
- Isomerization (Step 4): Straight chain proton substituted olefins convert to isomeric carbonium ions.
- Catalysts used: Acid catalysts (H₂SO₄) are used.
- Temperature: 150 – 220 oC are used. Too high temperatures give tar deposits.
- Pressure: 25 – 100 atms

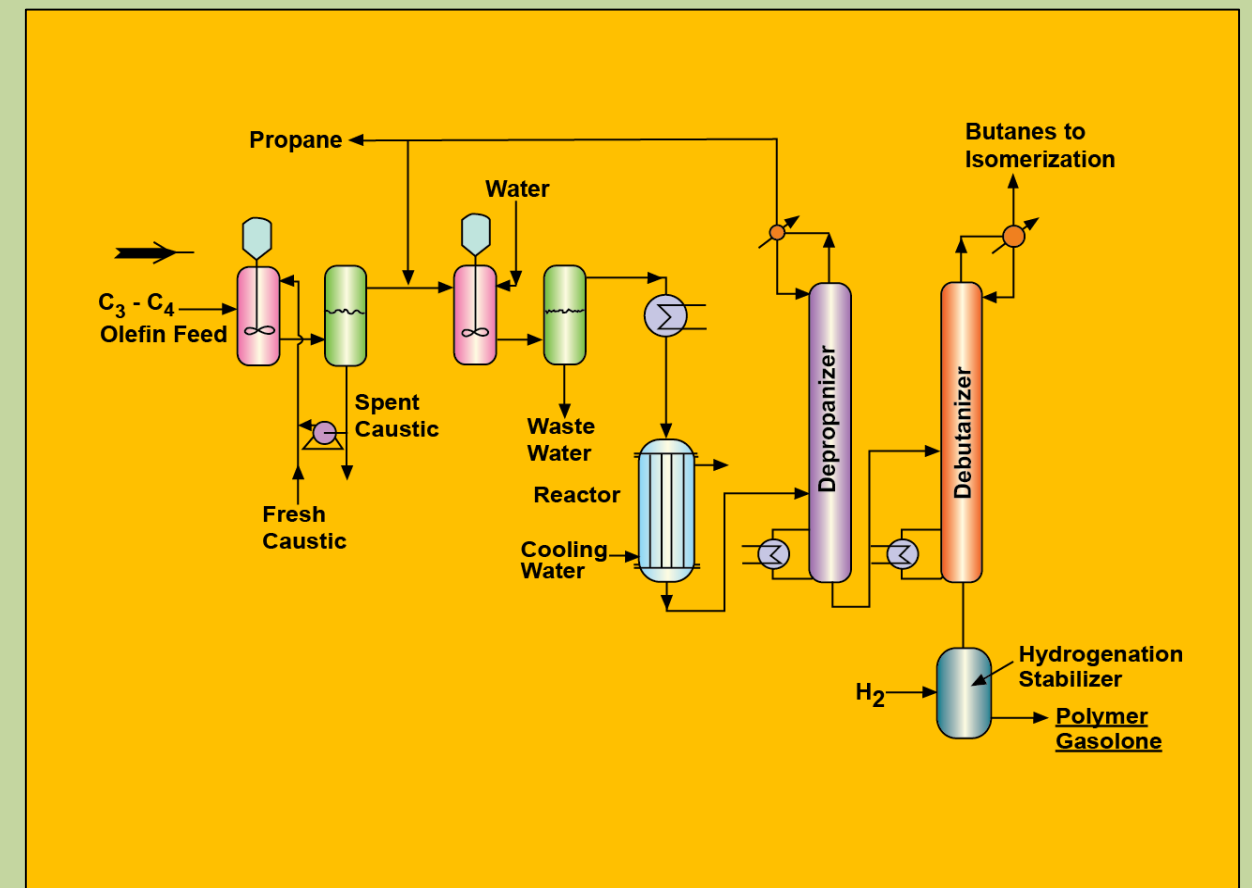
- Caustic wash: C3-C4 olefin feed subjected to caustic wash to remove H₂S and other sulphur compounds (such as mercaptans). These tend to poison the catalyst.

- **Water scrubbing:** Eventually water scrubbing is carried out to remove dissolved impurities and generate waste water.

- **Polymerization reactor:** The reaction mixture is heated, compressed and fed to a polymerization reactor. The reactor design is a shell and tube type design where catalyst is placed in the tube for the reaction to take place and cooling water is circulated in the shell side to control the temperature increase due to the exothermic reaction.

Fractionation: Subsequently, the reactor product is fed to a depropanizer and debutanizer to produce propanes, butanes and polymer gasoline. The polymeric product is further stabilization using hydrogenation stabilizer which converts any freely available double bonds to single bonds. The end product is polymer gasoline

- The propane produced is partially recycled to the reactor and the other part taken out as a product.



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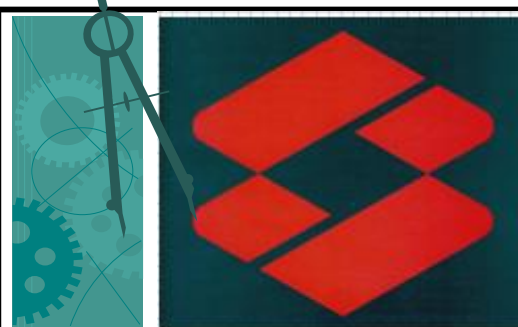
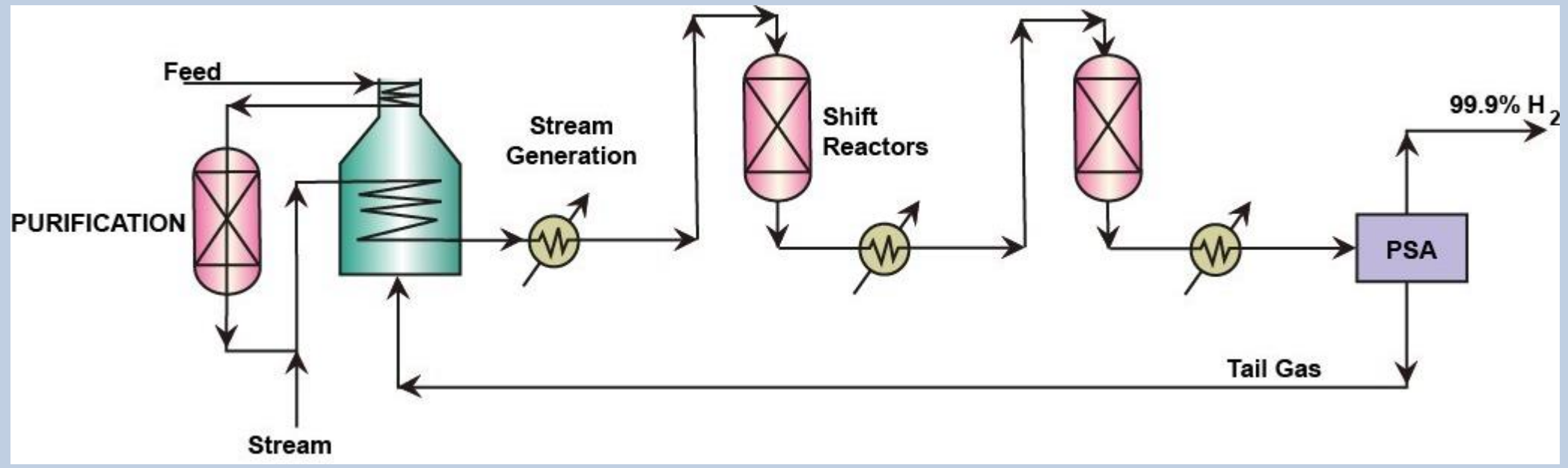
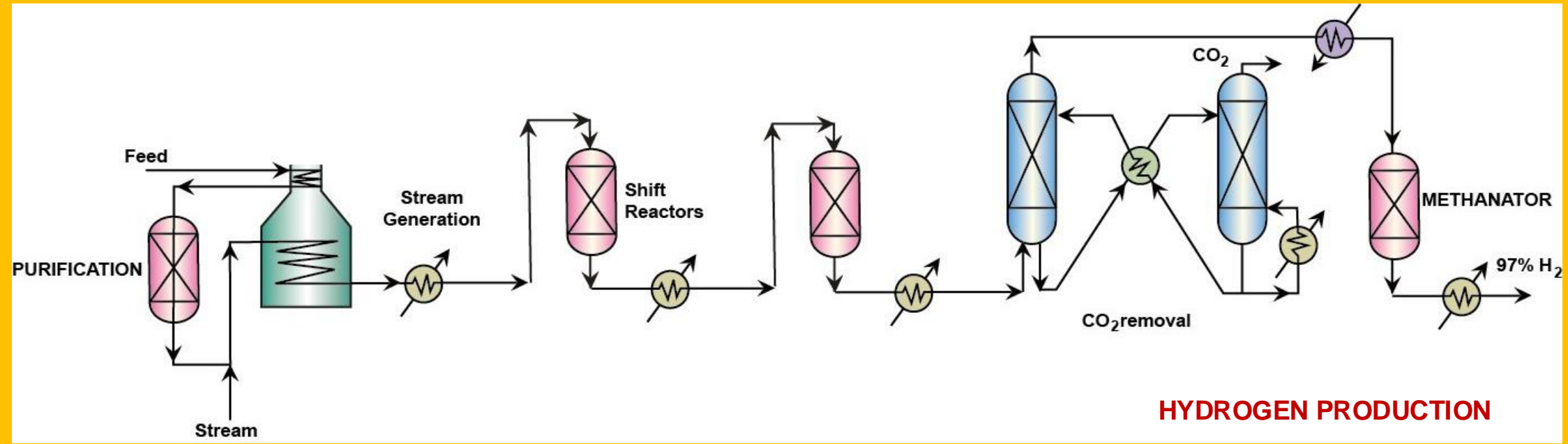
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REFINERY PROCESS-OTHER SUPPORTING PROCESS BASICS



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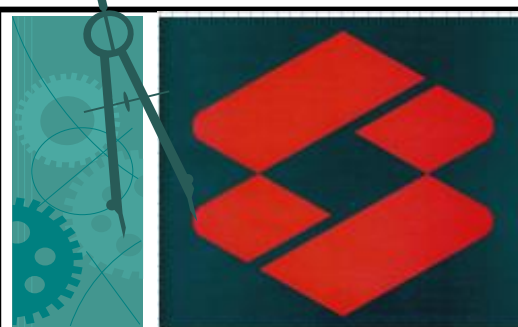
REFINERY PROCESS-OTHER SUPPORTING PROCESS BASICS

Introduction


- In this lecture, we present a brief overview of the refinery supporting processes.
- If we analyze the petroleum refinery, other than hydrocarbon balances, two other components balances need to be considered.
- These are sulphur and hydrogen.
- It is a fact that the refinery has good number of hydrotreaters which needs to be fed with hydrogen to generate the H₂S. This hydrogen is primarily generated from the catalytic reforming unit.
- Now the question that are posed in the refinery are
 - o How to handle H₂S for following environmental legislations
 - o How to purify the reformer H₂ gas stream to meet the required inlet specifications in various hydrotreaters, hydrocracking and isomerisation units.
 - o How to produce H₂ additionally, as the reformer off gas may not be able to meet the H₂ demands in various hydrotreaters.
- When the above question is answered, in due course, we get the two major supporting processes
 - o Hydrogen production and purification process
 - o Sulfur recovery process.
- We first discuss hydrogen production and purification process followed with the sulphur recovery process.

Hydrogen production


- Hydrogen can be produced in many ways namely
 - o Partial oxidation of heavy ends
 - o Steam reforming of various product stocks
 - o Methane steam reforming.
- Amongst these, methane steam reforming is more famous for hydrogen production
- Depending upon the process, the hydrogen production consists of four basic reactions
 - o Reforming: Here, methane reacts with water molecules to form CO and H₂ at about 20 bar and 800 oC. The reacton is endothermic.
 - o CO shift reaction: In this reaction, CO is converted to CO₂ and H₂ by reacting with water. The reaction is usually carried out on a catalyst. There are two types of shift reactions namely high temperature shift or low temperature shift. In the high temperature shift, the reaction is carried out on iron oxide or chromia catalyst at about 350 – 550 oC. In the low temperature shift, the reaction is carried out at 200 – 250 oC using copper or zinc oxide on alumina.
 - o Gas purification: The CO₂ is separated by passing the product gases through amine scrubber
 - o Methanation: The remaining CO₂ and CO are converted back to methane using nickel-alumina catalyst in a reversible reaction scheme at 400 oC.



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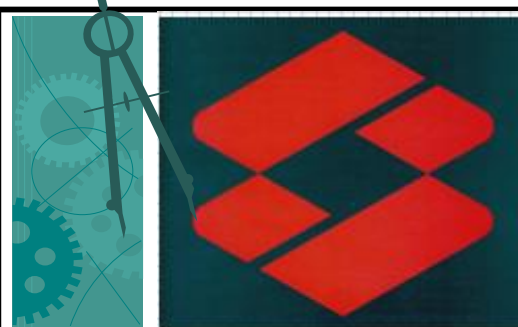
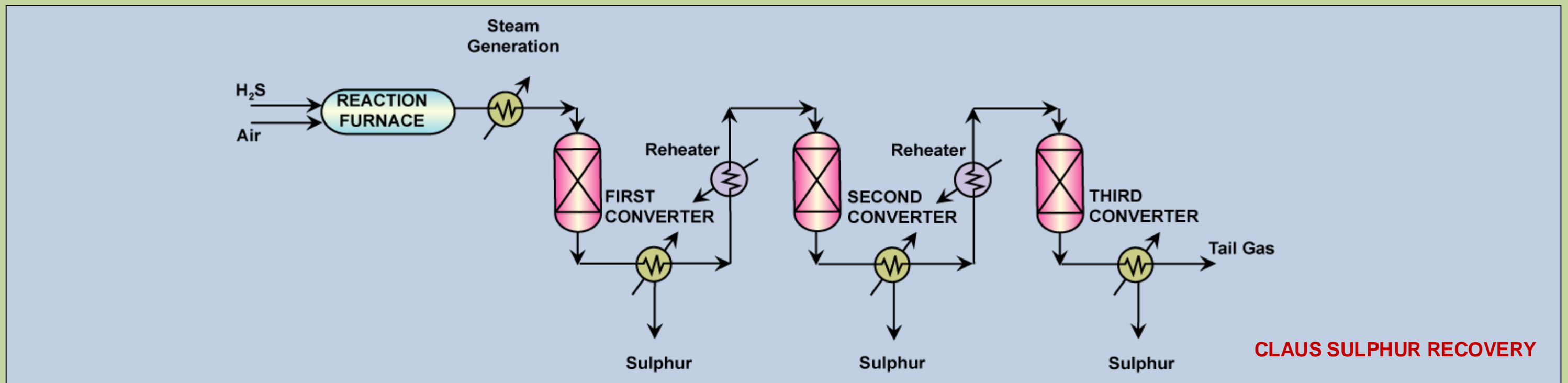
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REFINERY PROCESS-OTHER SUPPORTING PROCESS BASICS

- PSA technology also is incapable for CO and CO₂ removal as the adsorbents are not competent enough to separate these components to a large extent. But they can effectively do separation when hydrocarbons are present but not oxides in the hydrogen rich stream. Therefore, from PSA perspective as well it is important to remove CO₂ bulk with amine scrubbing followed with methanation reaction for both CO and CO₂ conversion.
- In a furnace reactor, H₂S is partially oxidized with air to produce water and SO₂. The reaction is highly exothermic. Therefore, steam is generated using the products from the furnace reactor.
- The remaining H₂S is then sent to a converter at about 250 °C to allow the reaction between H₂S and SO₂ and produce Sulfur and water. The emanating product is at 290 °C
- The second reactor (H₂S to SO₂) is having severe equilibrium limitations. Therefore, it is sent to two to three reactors for maximizing conversion.
- After each converter, the product stream is cooled and sent to another reactor.
- Subsequently, Sulphur is removed as a product from the coolers.
- Finally tail gas is obtained from the last converter which consists of unreacted H₂S, N₂ and O₂.
- The tail gas requires treatment as well. This is because the gas consists of components such as H₂S, CS₂ etc. The tail gas is fed with air to another burner and converter that converts sulphur compounds to H₂S. The H₂S thus generated is separated using amine scrubbers. The H₂S thus recovered is sent as a recycle stream to the partial oxidation reactor.



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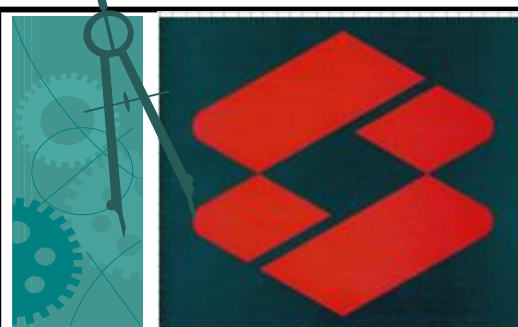
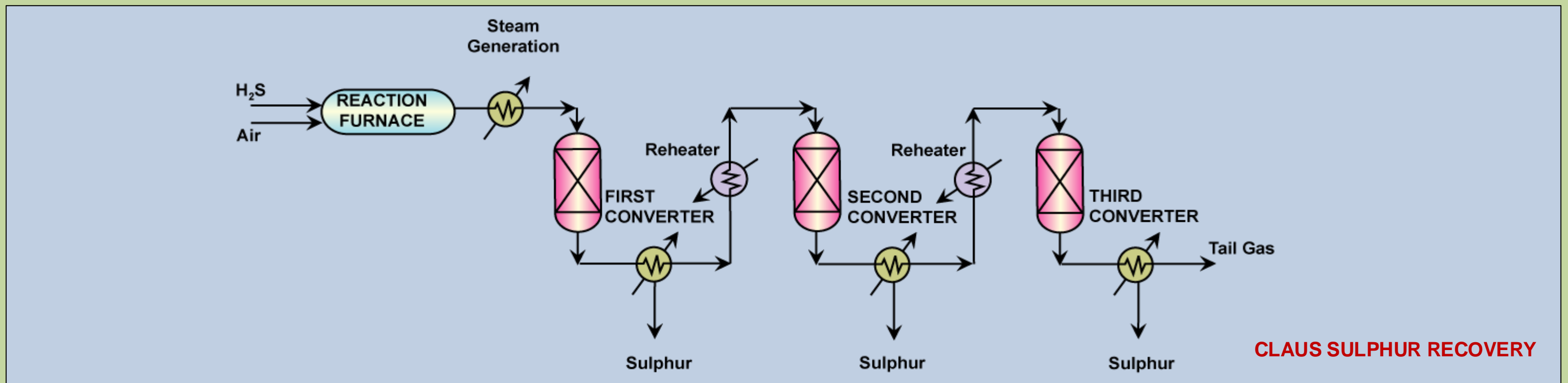
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REFINERY PROCESS-OTHER SUPPORTING PROCESS BASICS

- **Feed purification:** Feed pretreated to remove sulphur and halogens traces. H_2S is removed using zinc oxide catalysts. Organic sulphur removed by hydrotreating and H_2S removal from the feed. Halogens are removed using adsorption technique.
- **Furnace reactor:** The methane steam reforming reaction occurs in a furnace which is fed with the hydrocarbons mixed with steam. The steam to carbon ratio varies and is about 2.5 – 3.5. The furnace reactor consists of reactor tubes packed in the furnace chamber. The reactor tubes consist of the nickel oxide catalyst for carrying out the reaction.
- **Shift reactors:** The furnace reactor product is sent to both high temperature and low temperature shift reactors. It is interesting to note that these reactors operate at low temperatures. Therefore, cooling is carried out for the furnace reactor product and steam is generated. Similarly, steam is generated after the high temperature shift reactor also.
- **Absorber stripper:** The absorber stripper is used for CO_2 removal of the product emanating from the low temperature shift reactor.
- **Methanation reactor:** Here, traces of the CO_2 and CO are converted to CH_4 and H_2O using nickel catalyst and reversible reaction scheme. The product from methanation reaction consists of 97 % H_2 .
- Alternatively, in some modern refineries, the low temperature shift reactor product is fed to a pressure swing adsorption (PSA) unit which produces 99.9 % hydrogen as a main product.
- The PSA also produces a tail gas which is used as a fuel in the furnace used in the reformer process.



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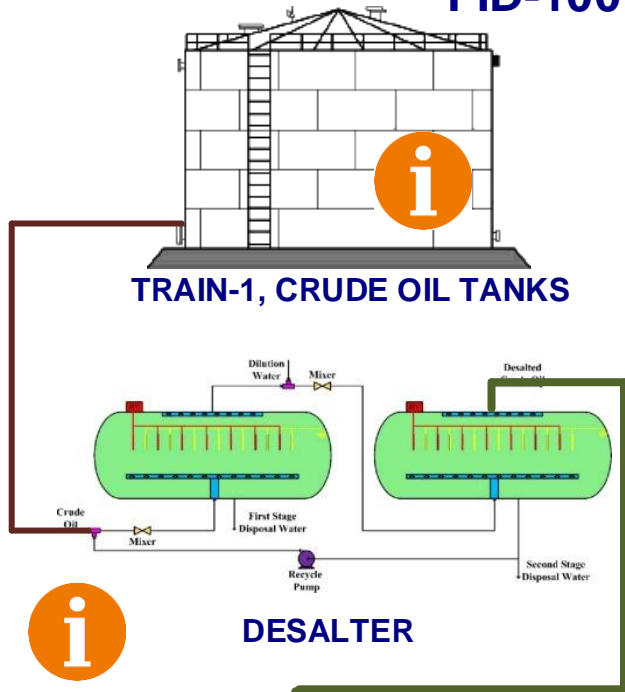
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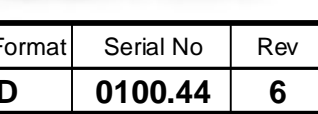
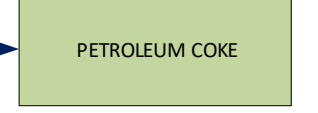
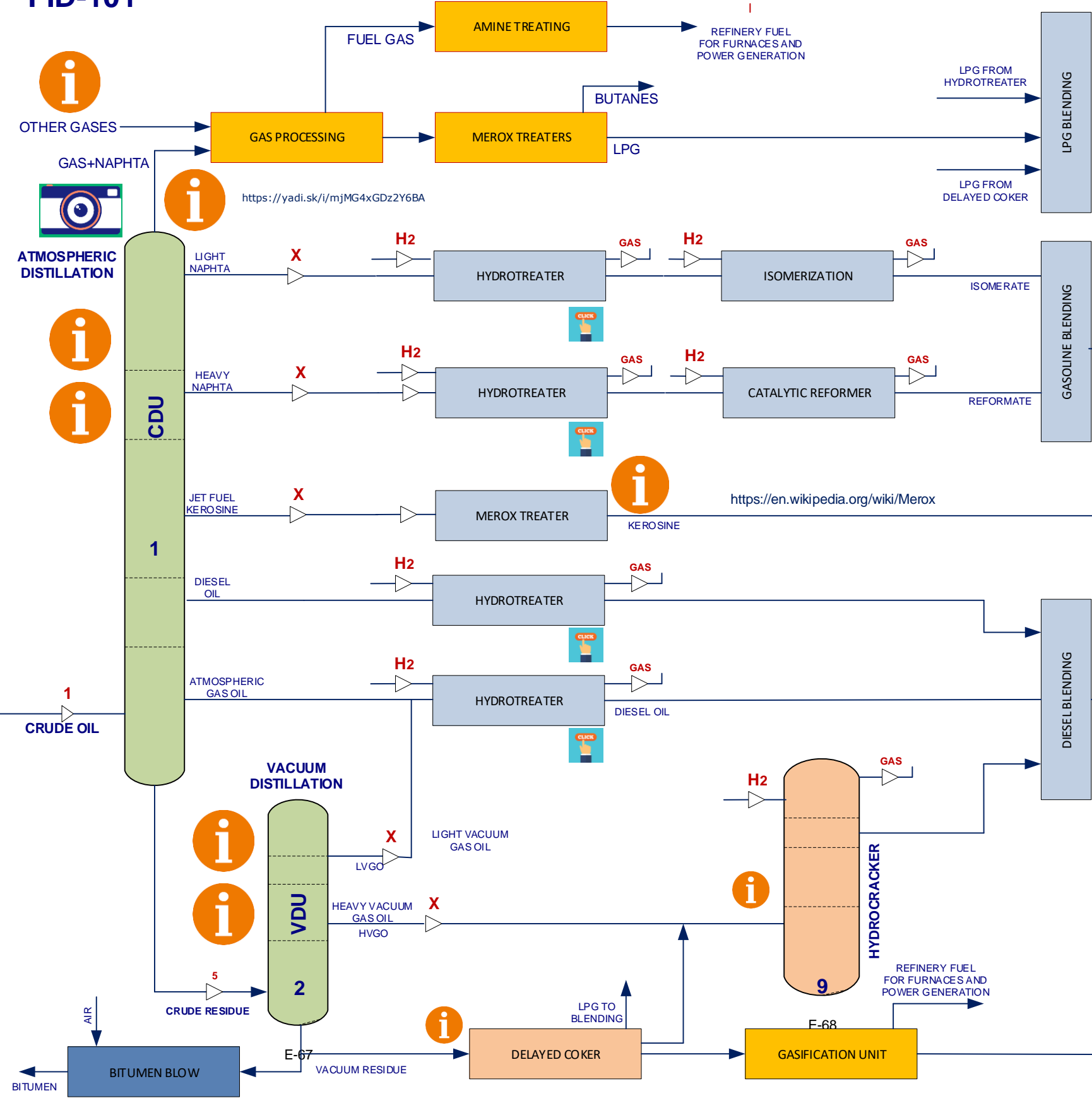


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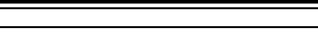
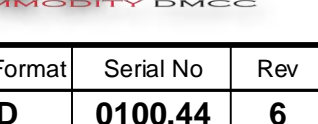
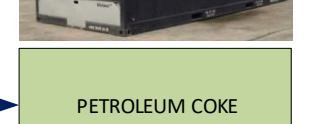
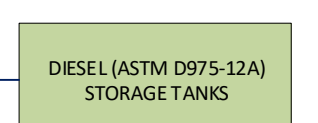
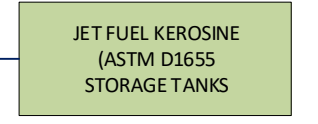
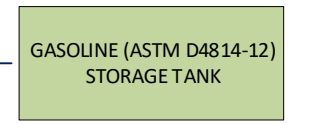
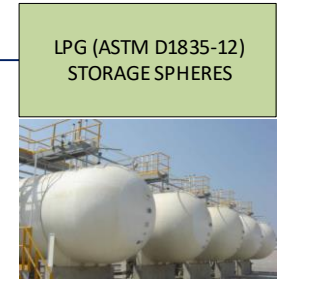
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