Module-3

Liquid Fuel

The important Liquide Fuel include diesel, oil, gasoline, liquid propane, alcohols etc. Most of the Liquid fuels (Hydro carbon fuels) are obtained by Refining petroleum or crude oil, which is very complex mixture. of components composed of many different types of hydrocarbon of various molecular weight.

Constitution of Petroleum (Crude Oil) :- Petroleum (crude Oil) consist of mainly carbon (83-87%) & Hydrogen (11-14%), Sulfur (0-3%) & Nitrogen (0-0.6%) having complex hydrocarbon mixture like paraffins, napthenes, aromatic hydrocarbon, gaseous hydrocarbons (from CH_4 to C_4H_{10}) gives more details about composition of petroleum. Besides crude Oil also contains small amount of non hydrocarbons (sulphur, Nitrogen, oxygen compounds) & minerals heavies crude contains higher Sulphur.

Crude Oil is costomarily characterized by the type of hydrocarbon compound that is most prevalent in them: Paraffins, Naphthenes & Aromatics. Paraffins are the most common hydrocarbon in crude oil, Certain liquid Paraffins are the major constituents of gasoline (petrol) & are therefore highly valued. Napthenes are an important part of all liquid refinery products, but they also form some of the heavy asphalt like residues of refinary process. Aromatics generally constitute only a small % of most crudes. The most common aromatic is crude oil is benzone, a popular building block in the petrochemical industry.

Crude oil is a mixture of such widely varying constituents & proportions, its physical properties also vary widely.

In appearance, for instance, it ranges from colourless to block.

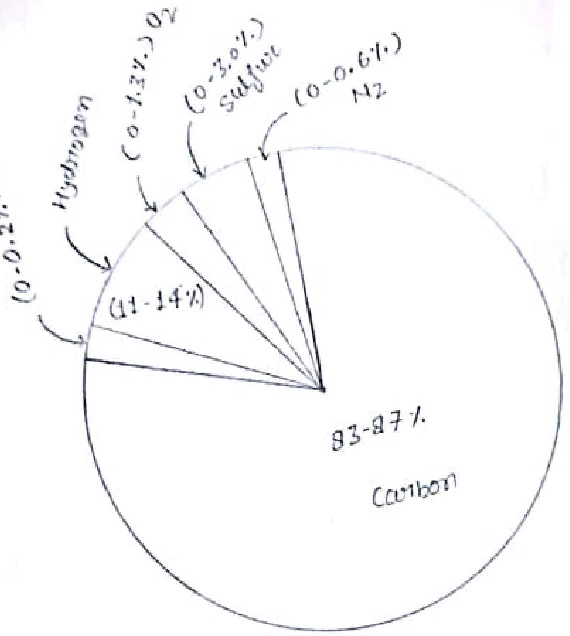


Fig 1: Elemental composition of crude oil

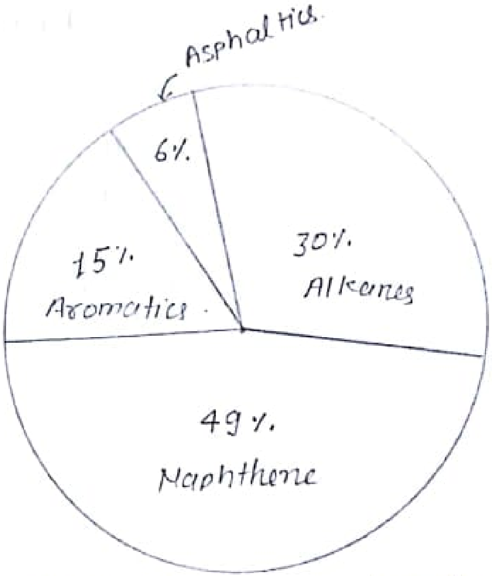


Fig 2:- Hydrocarbon composition of crude oil.

Characterization of Crude Oil

i) Nitrogen Content, wt%:- A high nitrogen content is undesirable in cr[illegible]e oil because organic nitrogen compounds cause severe poisoning of catalysed used in processing & cause corrosion problems such as Hydrogen blistering. Crude containing N_2 in amounts above 0.25% by weight require special processing to remove the N_2.

ii). Distillation Range:- The boiling range of the crude gives an indication of the quantities of the various product present. The most useful type of distillation is known as a true boiling point (TBP) distillation and generally refers to a distillation performed in equipment that accomplishes a resonable degree of fractionation. There is no specific test procedure called a TBP distillation, but th U.S. Bureau of mines Hempal & ASTM D-285 distillations are the tests most commonly used. Neither of these specify either the numbe of theoretical plates or the reflux ratio used and, as a result, there is a trend toward using the result of a 15:5 distillation (D-2892) rather than the TBP. The 15:5 distillation is carried out using 15 theoretical plates at a reflux ratio of 5:1. The crude distillation range has to be correlated with ASTM distillat ions because product specifications are generally based on the simple ASTM distillation test like D-86 & D-1160 etc.

iii). **Metal Content, ppm** :- The metals content metals (Nickel, Vanadium, & copper) of crude oils vary from a few parts per million to more than 1000 ppm. minute quantites of some of these metals can severely affect the activities of catalyst and result in a lower value product distribution. Vanadium concentrations above 2ppm in fuel oils can lead to severe corrosion to turbine blades and deterioration of refactory furnace linings and stacks. Distillation concentrates the metallic constituents of crude in the residues, but some of the organometallic compounds are actually volatilized at refinary distillation temperatures and appear in the higher-boiling distillates. The metalic content may be reduced by solvent extraction with propane or similar solvents as the organometallic compounds are precipitated with the asphaltenes and resins.

iv). **API Gravity** :- The density of petroleum oils is expressed in US in terms of API Gravity rather then specific gravity.

- It is related to specific gravity in such a fashion that an increase in API Gravity corresponding to a decrease in specific gravity.
- The units of API Gravity are API and can be calculated from specific gravity (sp. Gr.) by the following:

$$\text{API Gravity} = \frac{141.5}{\text{Specific Gravity}} - 131.5$$

- Sp. Gr. of crude oil may vary from less than 10 °API to over 50°API but most crude oil fall in the 20 to 45 °API range.
- API Gravity always refers to the liquid sample at 60°F (15.6°C).
- API Gravity are not linear & therefore cannot be averaged.

v). **Sulfur Content, wt%.** :- Sulfur content and API gravity are two properties which have the greatest influence on the value of crude oil, although Nitrogen & metal contents are increasing in importance. The sulfur content is expressed as % of sulfur by weight & varies from less than 0.1% to greater than 5%. Crudes with greater than 0.5% Sulfur generally require more extensive processing than those with lower sulfur content.

vi). **Pour Point** :- The Pour point of the crude oil, in °F or °C is a rough

Indicator of the relative paraffinicity and aromaticity of the crude. The lower the pour point, the lower the paraffin content & the greater the content of aromatics.

vii). Carbon Residue, wt%:- Carbon residue is determined by distillation to a coke residue in the absense of air. The carbon residue is roughly to the asphalt content of the crude and to the quantity of the lubricating oil fraction that can be recovered. In most cases the lower the carbon residue, the more valuable the crude. This is expressed in terms of the weight % carbon residue by either the Ramsbottom (RCR) or Conradson (CCR) ASTM test procedures.

viii). Salt Contents, lb/1000bbl:- If the salt content of the crude, when expressed as NaCl, is greater than 1[illegible]lb/ 1000bbl, It is generally necessary to desalt the crude before processing. If the salt is not removed, severe corrosion problems may be encountered. If residua are processed catalytically. desalting is desirable at even lower salt contents of the crude. Although. it is not possible to have an accurate conversion unit between lb/1000bbl and ppm by weight because of the different densities of crude oils, 1 lb/1000bbl is approximately 3 ppm.

ix). Characterization Factors:- There are several correlations between yield and the aromaticity & paraffinicity of crude oils, but the two most widely used are the UOP or Watson "Characterization factor" (Kw) & the U.S. Bureau of mines "correlations index" (CI).

$$K_W = \frac{T_B^{1/3}}{G}$$

$$CI = \frac{87,552}{T_B} + 473.7G - 456.8$$

where,

T_B = mean average boiling point °R

G = specific gravity at 60°F

- $K_W \sim 15$ for highly paraffinic compounds, $K_W < 10$ for highly aromatic materials & K_W vary from 10.5 to 12.9 for a highly naphthenic crude

⇒ Theory of formation of crude:- There are two theory of formation of crude oil.

i). Inorganic Theory:- Inorganic theory of the origin of the petroleum states that hydrogen and carbon came together under great/high temperature & pressure. far below the earth's surface and formed oil & gas. The oil & gas then seeped throug porous rocke to deposit in various natural underground traps.

ii). Organic Theory:- Organic theory is the one of most widely accepted. According to organic theory, the oil & gas are formed from remains of prehistoric plants and animals. Remains of plants have been transformed to coal & animals's to oil & gas. This remains were settled in to seas and lands along with sands & slits, mud and other minerals. As the rock and slit settled, layer upon layer piled into rivers, along coastlin and on the sea bottom.

Geological shifts resulted in some of these layers being burried deep in the earth. over the time, the layer of the organic material were copressed under the weight of the sediment above them. The increase in pressure and Temperature changed the mud, sand, slit in to rock & organic matter in petroleum. The rock conteining the organic matter that turned into petroleum is reffere as Source Rock.

⇒ Operation and flow-sheet of crude distillation:- The first essential task for the crude oil consisting of more than 10^8 Compound is to separate its major component based on boiling point differences. The principal is explained 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 refinary.

The conceptual process flowsheet for the petroleum refinery is shown in the figure 3 It consists of the following important sub-process.

i). Crude desalte   ii) Furnace

iii). Pre-flash Column

iv). Crude distillation column supplemented with side column. These columns produce the desire product.

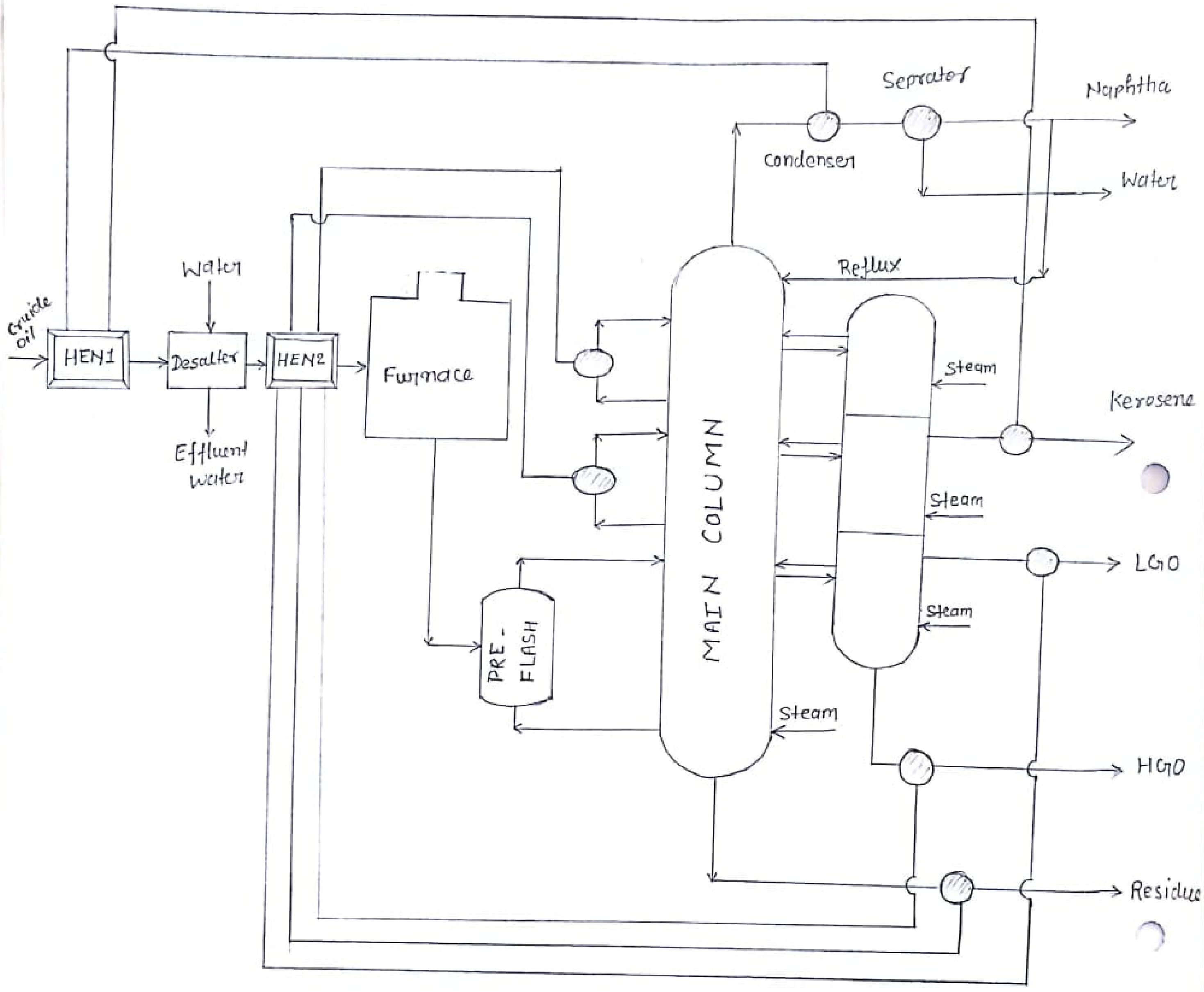


Fig 3:- Process flowsheet -a conceptual diagram of the crude distillation unit(CDU) along with heat exchanger network(HEN)

v). Pump around heat Exchanger units.

vi). Heat Exchanger network that facilitates energy recovery from hot product and reflux steams to heat the crude oil.

vii). We next present the functional role of various sub-processes in the crude distillation unit.

i). Crude Desalter:- • Crude oil consist of dissolved salts & they tend to Cause fouling and corrosion in various process equipments. Therefore dissolved salts need to be removed using a

Sepration process.

- The crude desalting unit is a sepration 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.
- The mixture of crude oil and water is ssbsequently 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 temp. of the operation. Usually, high efficiency of salt removal is possible between 100°- 300°F.
- Therefore, the crude oil is heated to about 250°F 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 impurties 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 developed. When higher salt removal efficiencies are desired, three stage units are deployed.

ii). 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 temp.
- Typically in refineries, the crude oil is heated to a temperature that enables overflash conditions in the main crude oil temperature. distillation column.
- The concept of overflash is that the crude is heated to such a temp. that enables an additional 5% vaporization w.r.t. the residue products. In other words, the residue fraction vapour 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°F.

iii). 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 emanting 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.

iv). Main & secondary distillation Columns :- • The distillation columns consisting of both main & secondary crude distillation columns are one of the most complex circuities in distillation.

- The complex arrangement of distillation columns is based on research carried out with pilots plants & simulations software.
- The crude distillation columns (both main & primary) are regard to an indirect sequence of thermally coupled distillation sequences to obtained the desired products.
- Effective distilbution of vapour & reflux in the main column is a serious issue
- The effective distribution of vapour & 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 principal of using live steam out from several facts. Firstly, upon condensation, oil and water are very easy to seprate. Secondly, steam can take significant amount of heat in terms of enthalpy Thirdly, steam enables enhacement in relative volatility, a pricipal

that is used in steam distillation laboratory experimental setups. These principals 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 volatilities of the hydrocarbones at various sections of the main & secondary towers.
- Therefore, live steam still 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 vapour.
- 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.

v). Pump - around Units :-
- Pump around units are most essential unit in the crude distillation column.
- They are used to maintain good reflux conditions in the main column and therfore the desired product quality.
- They also provide a good heat exchanger source as the liquid steams are at higher temp. Therefores, 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 & secondary towers along with relevant pump around units are presented in Fig. 2. It can be seen that very complex interactions exists between the main & secondary columns.

a). The main column consist of 45 trays and the secondary columns (side strippers) consist of 4 tray each. Three sides strippers are used to strip the light end from kerosene, LGO & HGO products

(b). The main column has two sections that are distinguished w.r.t a flash zone. The flash zone is where the crude oil partially vaporized is fed to the main column. There are about 4 tray 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 & the top tower tray is numbered as 45 Tray 1 to 4 process the atmospheric residue portion of the crude in the section below the flash zone.

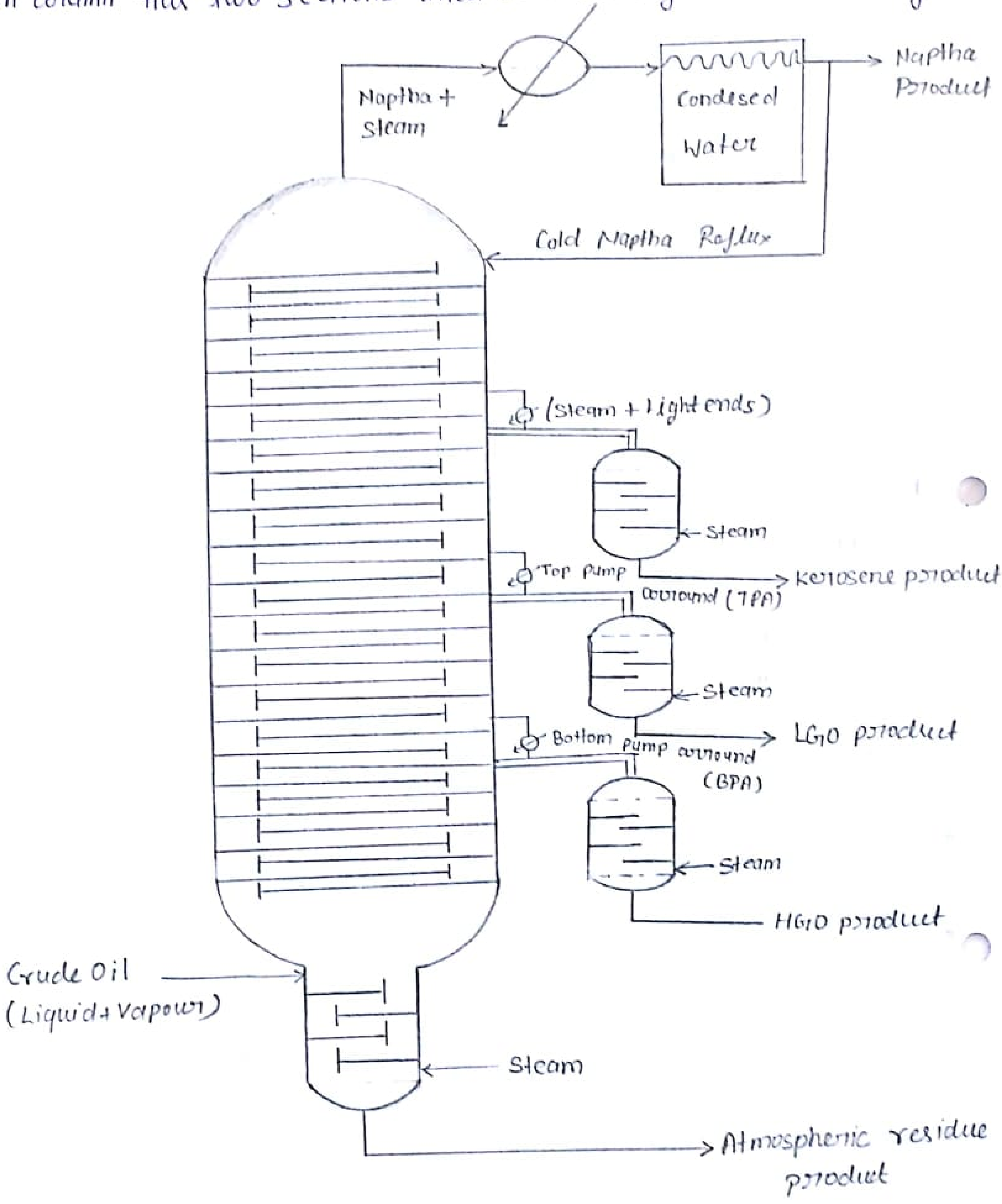


Fig 2: Design Architecture of main & Secondary columns of the CDU

c). Tray 5 to 10 (6 tray 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 steam. The steam + light ends from the HGO side stripper enter tray 11 of the main column.

d). Tray 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) & sent to the LGO side stripper unit, Also, from tray 22, another liquid steam is taken out & sent to tray 24 via a top pump around unit (TPA) that enables coling of the liquid steam. The steam + light ends from the LGO side stripper enter tray 23 of the main column.

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

f). Tray 35 to 45 (12 trays above the Kerosene processing zone) proces 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 naptha 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 affect 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 tray 1, 11, 23, 35 & therefore is present along with the vapour steam along with the hydrocarbons. Therefore, steam balances throughout the column are very important.

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

vi). 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 vapour & reflux streams to heat the crude oil in an indirect heat transfer mode i.e. using heat exchanger.
- Therefore, the design and operation of a heat exchanger network is very important in the crude oil distillation unit.
- Further, it needs to be understood that the naptha 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 steam temp. to about 200-230°C which is significantly higher than the crude oil source temp. (about 20-30°C)
- Crude distillation units without heat exchanger networks higher furnace load targets. They also cause move pollution due to burning more fuel oil & fuel gas streams.

⇒ Cracking:- • Cracking involves the decomposition of heavier hydrocarbon feedstock to lighter hydrocarbon feed stocks.

- Cracking can be carried out to any hydrocarbon feedstock but it is usually applied for vaccum gas oil (VGO).
- Cracking can be with or without a catalyst.
- When cracking is carried out without a catalyst higher operating temp. & pressures are required. This is called as thermal cracking.

⇒ Cracking Chemistry:- • Long chain paraffins converted to olefins and olefins
- Straight chain paraffins converted to branched paraffins

- Alkylated armotics converted to aromatics & 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 reactions.

Therefore in principal 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 & less coke formation.
- For vaccum gas oil, thermal cracking requires operating at 600°C & 20 atms gauge pressure.

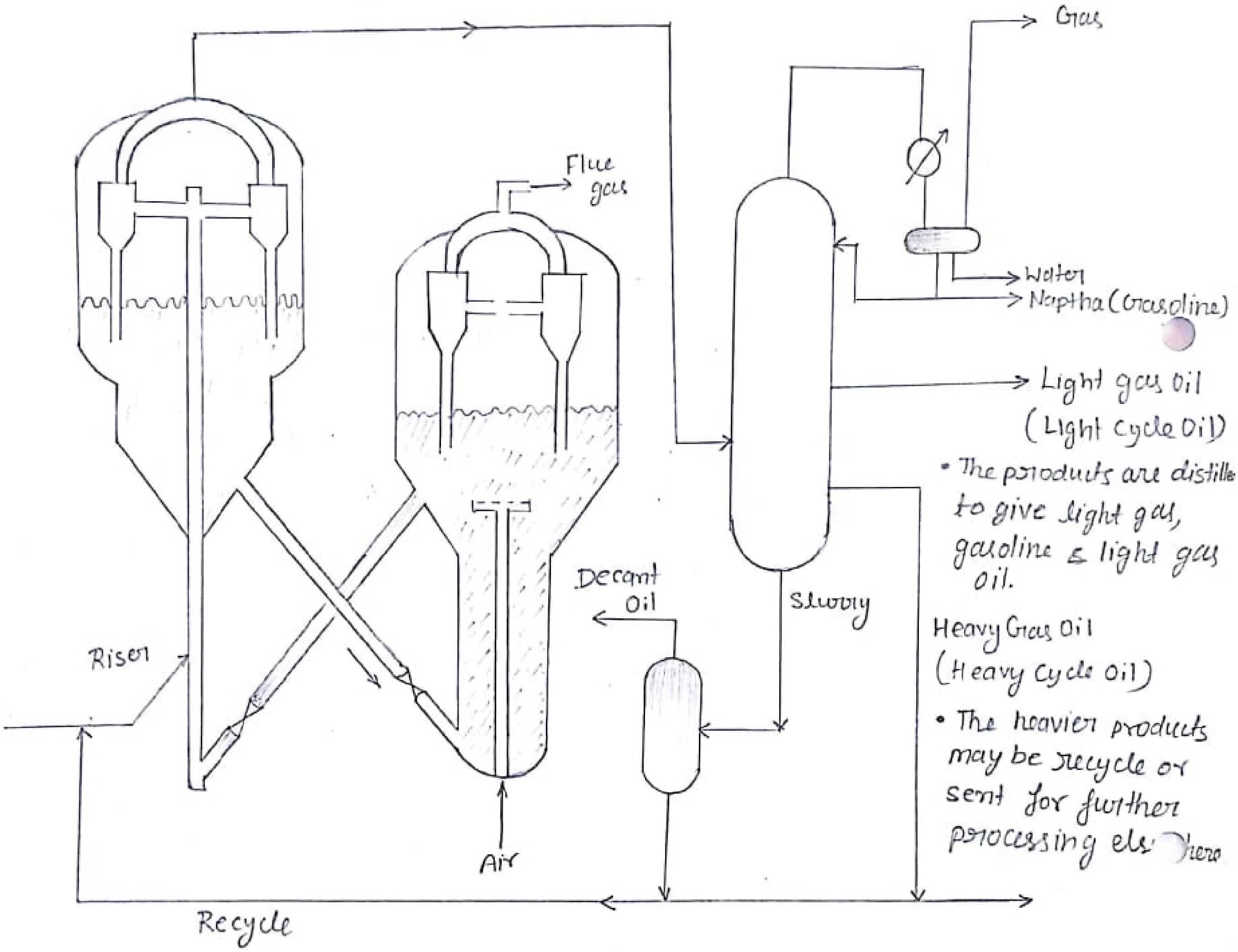
⇒ Catalyst:- • Acid treated silica - Alumina was used as catalyst.

- 20-80 mesh size catalyst used for FCCR & 3-4 mm pellets used for MBRs.
- During operation, poisoning occurs with Fe, Ni, Vd & Cu.

⇒ Catalytic Cracking:- Catalytic cracking breaks complex hydrocarbon into simpler molecules in order to increase the quality & quantity of lighter, more desirable products & decrease the amount of residuals. This process rearranges the moleculer structure of hydrocarbons compounds to convert heavy hydrocarbons feed stock into lighter fractions such as; kerosene, Gasoline, L.P.G, & petrochemical feed stocks. Use of a catglst in the cracking reaction increase the yield of improved-quality products under much as severoperating conditions than in the thermal cracking.

⇒ **Catalytic Cracking : Process Technology :-** The process technology consist of two flowsheets namely the cracking coupled with main distillation column & stabilization of naphtha.

- * Feed enters the cracking reactor.
- * Old generation refineries used moving bed reactors.
- * Now a days fluidized catalytic cracking (FCC) reactors are used.



• The products are distille to give light gas, gasoline & light gas oil.

• The heavier products may be recycle or sent for further processing els[illegible]here

Fig 3:- Flow Sheet of Catalytic Cracking Process

- * The cracked product from the reactor enters a main distillation column that produces unstabilized naphtha, light gas oil, heavy gas oil, slurry & gas.
- * The naphtha obtained is unstablized, as it consist of various hydrocarbons. It is therefore subjected to stablized by continued processing.
- * The slurry enters a phase separation unit which separates decant oil & 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 seperator separates lighter hydrocarbones from heavier hydrocarbones.

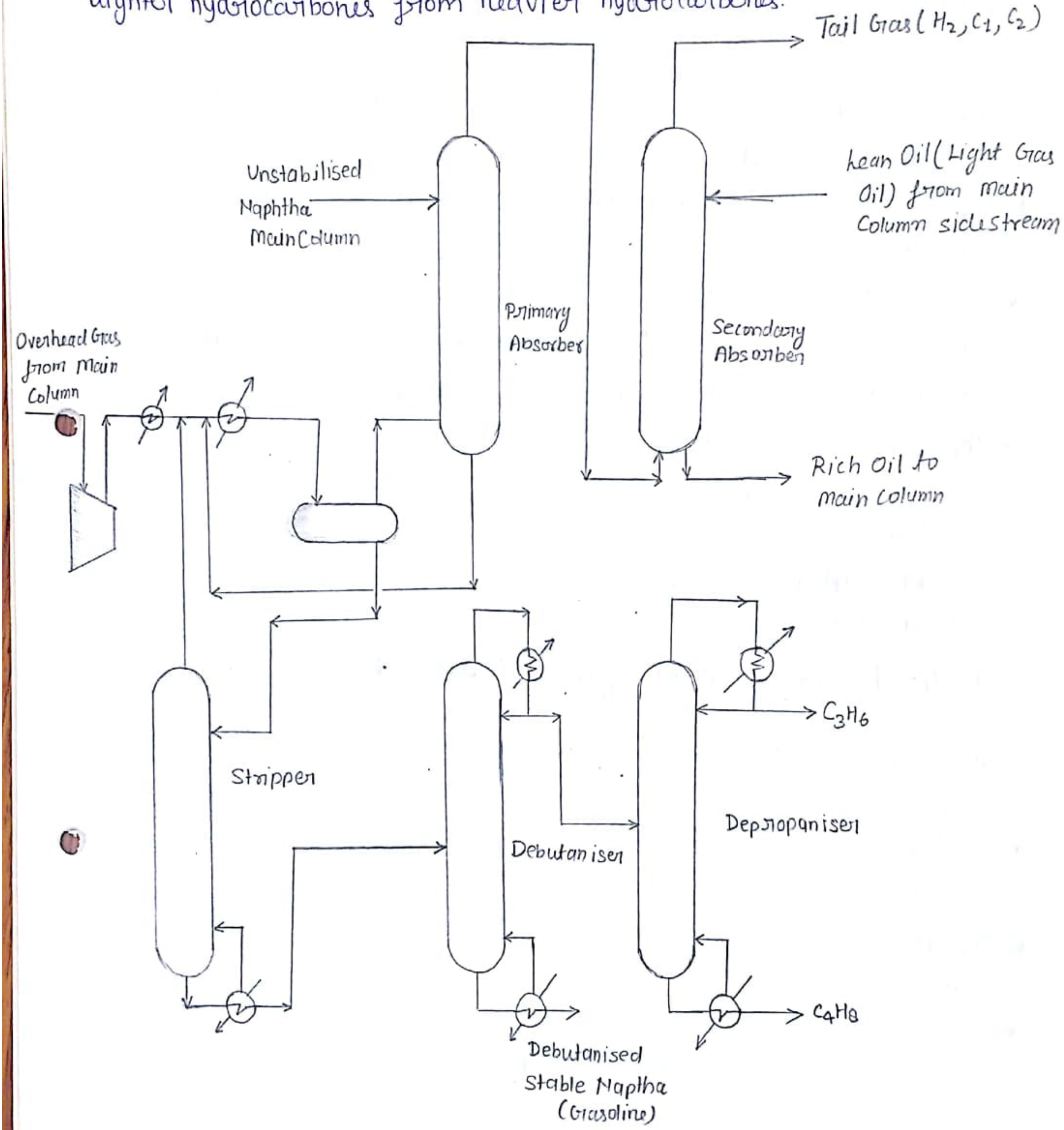


Fig4:- Naptha Stabilization flowsheet.

- The phase seperator is also fed which the unstabilized naphtha. The unstablized naphtha from the main column is first fed to a primary absorber to absorb heavier hydrocarbones 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 form main distillation column is used as a absorber to further extract any absorbable hydrocarbons into the light gas Oil. Eventually, the rich light gas oil enters the mains distillation Column (not show in the fig.a).
- The naphtha generated from the phase separator is sent to stripping to further consolidate & stabilize naphtha.
- The stabilized naphtha is further subjected to distillation in debutanize and depropanizer units.
- The debutanizer unit removes butanes & lower hydrocarbons from the Naphtha. The naphtha obtained as bottom product in the debutanizer is termed as debutanized stable naphtha or gasoline.
- The butanes & other hydrocarbones are sent to a depropanizer unit where butanes are separated from propanes & other lighter hydrocarb nes. Thus, butanes are obtained as lower product & propanes along with other lighter hydrocarbones are obtained as the top product in the depropanizer unit.

⇒ **Fluidized Catalytic cracking Reactor (FCCR)** :- * The basic principal of the FCCR is to enable the fluidization of catalyst particles in the feed steam at desired pressure & temperature.

- Another issue for the FCCR is also to regenerate the catalyst by burning off the coke in air.
- Therefore, the reactor unit should have basically two units namely a reactor (FCCR) and a catalyst regenerator (CR)
- The FCCR consists essentially of two important components in a sophisticated arrangement. These are the riser & the cyclone unit assembled in a reactor vessel.
- Riser : In the riser (a long tube), the feed is allowed to get in contact with the hot catalyst. The hot catalyst is enabled to rise and the cyclone unit assembled in a reactor vessel.
- The hot catalyst is enabled to rise through lift media in the riser. The lift media is usually steam or light hydrocarbon gas.

* The riser contact time is about 250milliseconds.
* The riser eventually connected to cyclone units.
* The cyclone units receiver the catalyst & finished product. The catalyst that enters the cyclone unit is fully coked & needs to be sent to a regenerator to regain its lost activity.
* After cyclone operation (which seperatores the hydrocarbon vapors & catalyst as a solid fluid operation), the catalyst falls down to the vessel that houses the riser & cyclone units.

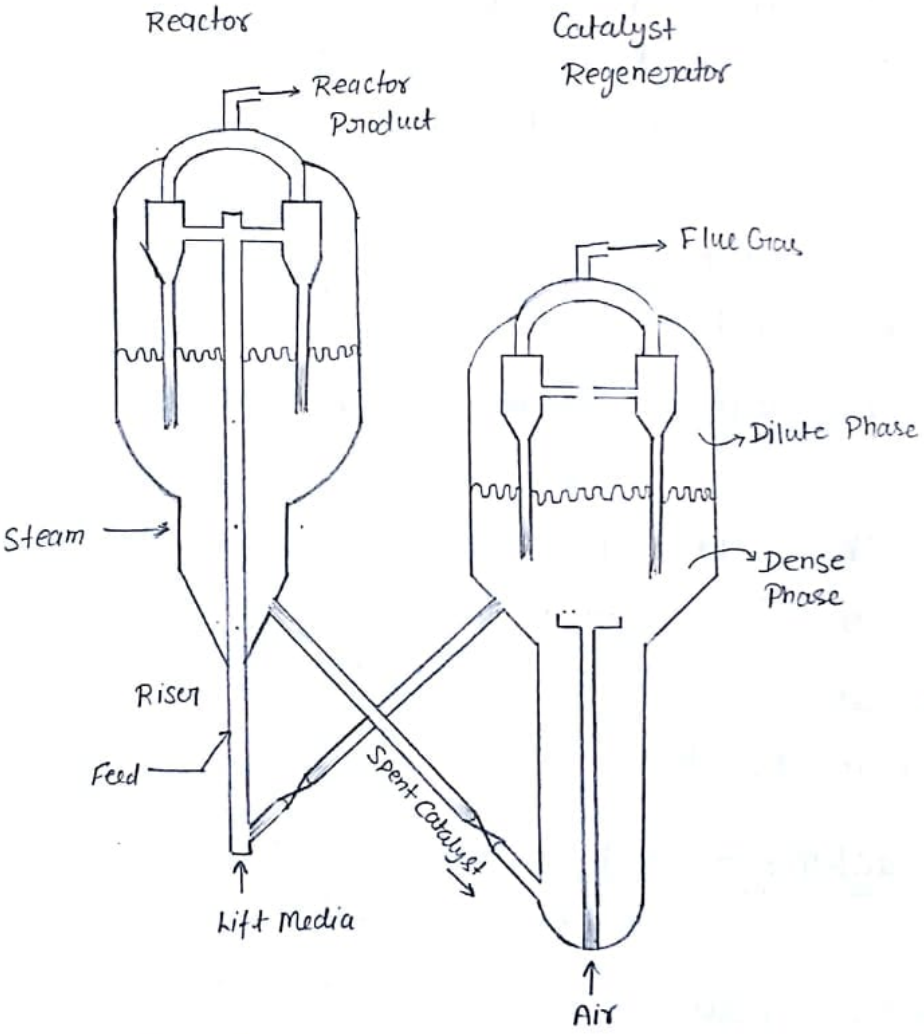


Fig:5 Fluidized Catalytic Cracking Reactor

* The catalyst in the vessel is subjected to stream stripping in which direct contanct with steam is allowed to remove hydrocarbones from the catalyst surface.

⇒ Catalyst Regenerator (CR):- * The spent catalyst which is relatively cold enters the regenerator unit.

* Here air enters the vessel through a sparger setup.
* The catalyst is subsequently burnt in the air. This enables both heating the catalyst (which is required to carry out the endothermic reaction) & removing the coke so as to region the activity of the Coke.
* The catalyst + air after this operation will enter the cyclone separator unit. Unlike the FCCR, the CR does not have a riser. Therefore, air enters a dense phase of catalyst & also enables the movement of the catalyst to a dilute phase of catalyst + air.
* The cyclone seperators separate the flue gas & catalyst as a solid fluid operation.
* The activity regained catalyst is sent to the riser through a pipe.
* Durining the entire operation, the catalyst temp. is increased to 620-750 °C.
* The flue gas is obtained at 600-760°C & is sent for heat recovery unit to generate steam.

⇒ Thermal Cracking :- The first thermal cracking process was developed around 1913. Distillate fuels and heavy oils were heated under pressure in large drums until they cracked into smaller molecules with better antiknock characteristics. However, this method produced large applications of thermal cracking:

- Visbreaking
- Steam cracking
- Cooking.

* Simple thermal cracking process produces gas, naphtha, middle distillates and thermal tar from almost all variety of charge stocks from distillates to the heaviest crude & residual oils.

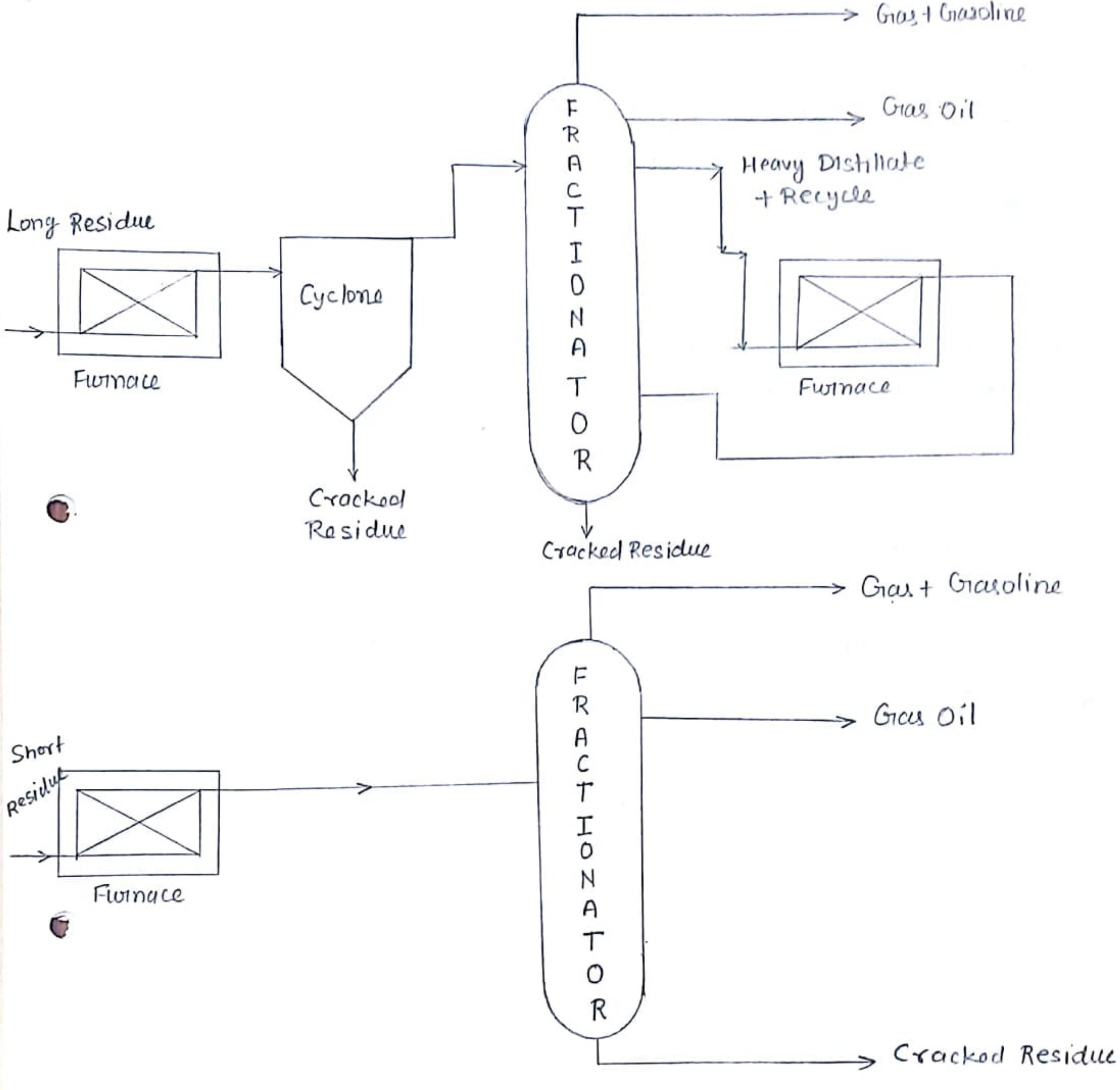


Fig 6: Thermal Cracking Process, Long Residue & Short Residue

* The feed is heated to cracking temperature 450°- 500°C and the cracked productes containing gas and Full Boiling Range distillates enters the fractionators after passing through an intermediates separator vessel.

⇒ **Visbreaking Process :-** • Visbreaking is a mild thermal cracking process & help in reducing the viscosities & pour point of long to short residues. Refinery productions of heavy oils can be reduced by 30% using visbreaking process.

- Visbreaking produces Naphtha, Gasoil & a residue. The residue has lower viscosity & pour point & hence can easily meet the requirment of the fuel oil specifications in the fuel oil blending pool.
- Visbreaking basically breaks the long paraffins side chains attached to aromatic structures. Due to this the residue pour point & viscosities are considerably reduced.
- Two classes of reactions occur during visbreaking.
  - i). Cracking of side chained aromatic compounds to produce short chained aromatics & paraffins.
  - ii). Cracking of large molecules to form light hydrocarbons.

⇒ **Process Technology :-**

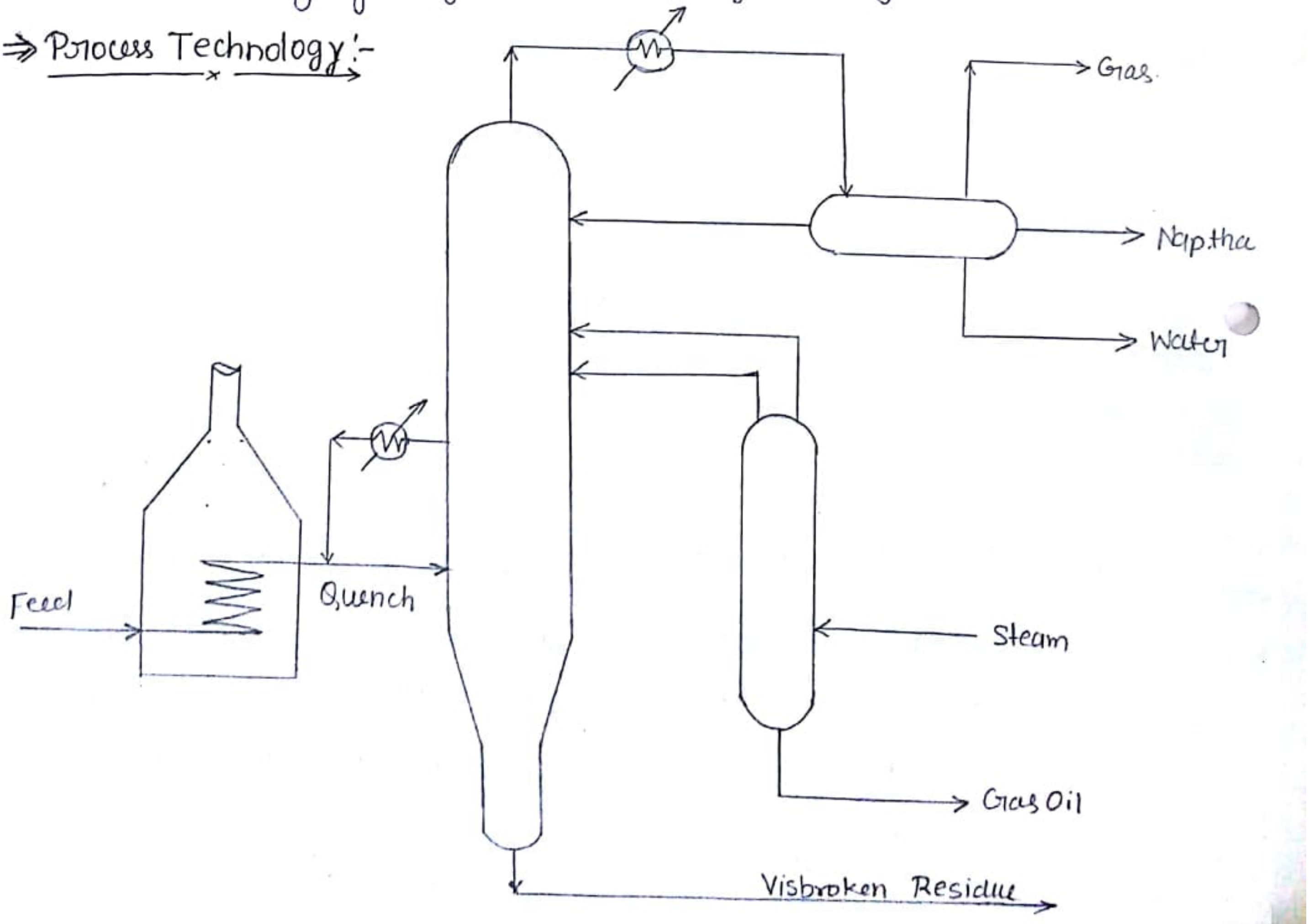


Fig 7: Visbreaking Process Flow sheet.

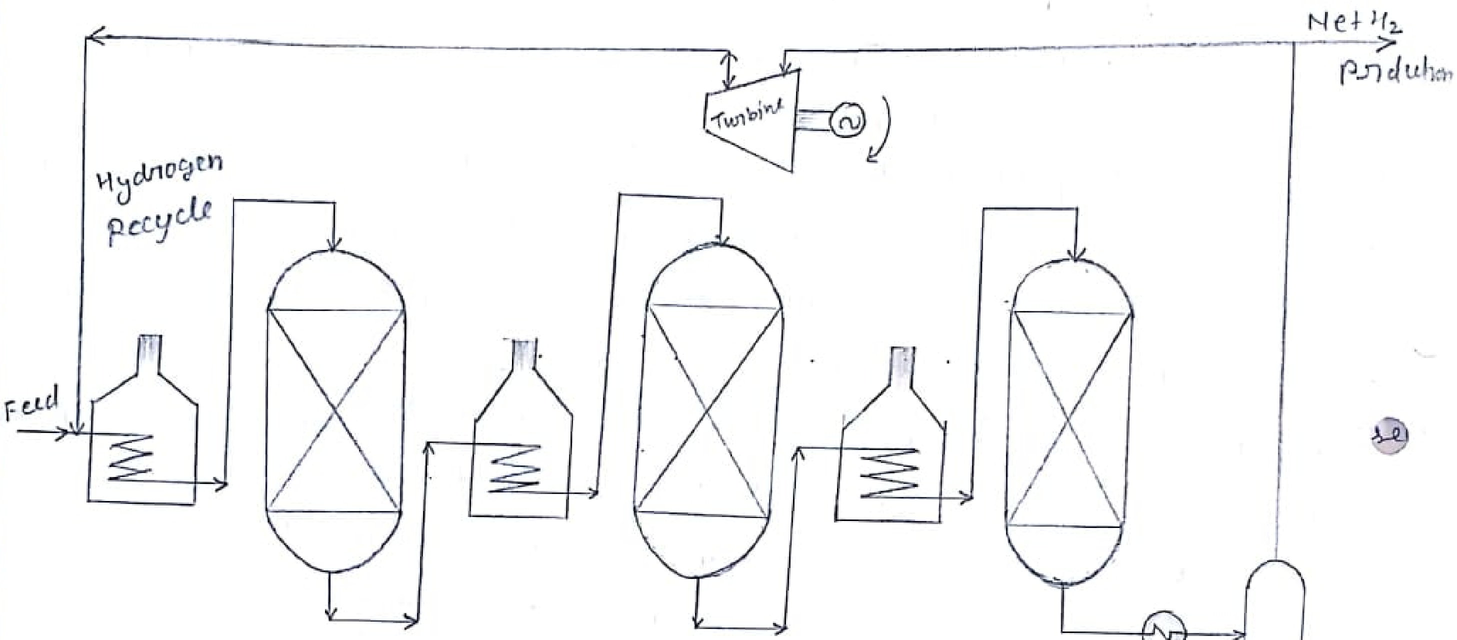
- Visbreaking is caried out either in a coil or in a soaker.
- When coil technology is used, the mild thermal cracking is carried out in the furnace coils.
- When soaker technology is adopted, the cracking is carried out in a soaker unit that is kept immediately after the furnace.
- After cracking, the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

⇒ **Reforming Process :-** Reforming is a major conversion process in petroleum refinery & petrochemical industries. The reforming process is a catalytic process which converts low octane naphthas into higher octane reforming products for gasoline blending & aromatics rich reforming for aromatic production. Basically, the process re-arrange or re-structure the hydrocarbon molecules in the naphtha feedstock as well as breaking some of the molecules into smaller molecules. Naphtha feeds to catalytic reforming include heavy straight run naphtha. It transforms low octane naphtha into high-octane motor gasoline. blending stock & aromatics rich in benzene, toluene & xylene with hydrogen & liquified petroleum gas as a byproduct with the fast growing demand in aromatics & demand of high-octane numbers, catalytic reforming is likely to remain one of the most important unit process in the petroleum & petrochemical Industry

⇒ Process Technology :- * The feed is mixed with recycle hydrogen

* Subsequently, it is heated before sending to reactor

* Since the reaction 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 principal 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 steam from liquid steam.

* The liquid steam from the phase seperator is sent to a debutanizer distillation column that seprates butanes and lower alkanes from the reformate products.

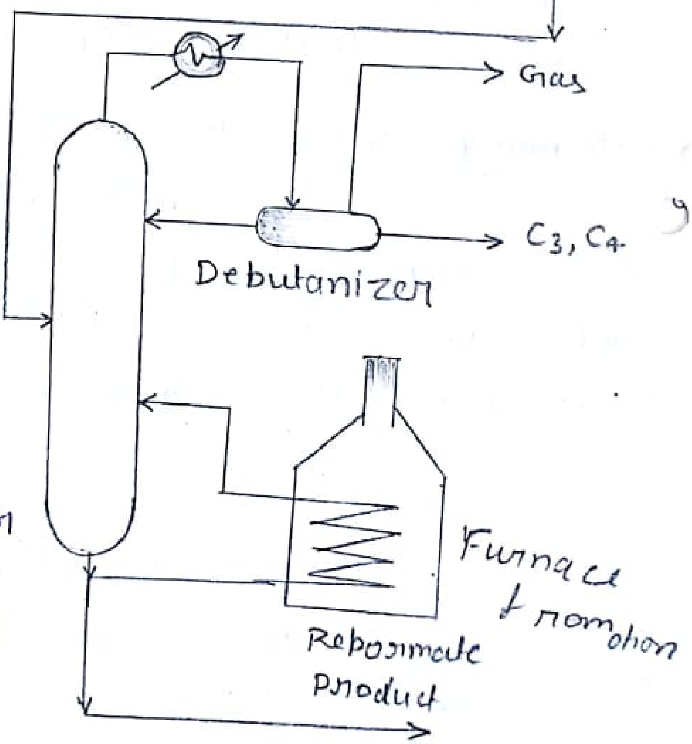


Fig: Flow sheet of Reforming Process.

* Excess hydrogen produced in the phase seperator is compressed and sent back to first reactor.

* Excess hydrogen generated in the reactions is taken out as a bleed steam

* Catalyst regenration (not show in the flow sheet) needs to be carried out to regain catalyst activity. This can be in different mode of operation namely cyclic, semi-regenerative or continuous. When continuous mode of Catalyst regeneration is carried out (as UOP continuous catalytic reforming process), the moving bed designs are used for the reforming reactor. Additional complexity in the moving bed reactors is to be enable process intensification to club the sequences of three reactors is to enables + heater into one single unit.

** Hydrogen reduces the coke formation on the catalyst and therefore increase the shell life of the highly expensive platinum catalyst so hydrogen used in the reforming process. reaction.

⇒ Coking Processes:- Coking is a severe method of thermal cracking used to upgrade residuals into lighter products or distillate. Coking produces straight liq/ rum gasoline (coker naphtha) and various middle-distillate fractions used as catalytic cracking feedstock. The process so completely reduced hydrogen that the residue is a form of carbon is called "coke". The two most common process are

i) Delayed Cocking Process
ii). Continuous (contanct or fluid) Coking process.

i) Delayed Coking Process:- The heated feed is fed to a coke drum and coke form 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 & it is then removed using waterjets. The process is called delayed coking because in this process the coal is heated using a much more complex system and it consist of multiple furnaces or coke drums. Usually the coal is heated at a lower temp. for shorter period of time, which removes water & other by-produts more slowly than the conventional process, there by increasing the overall time span.

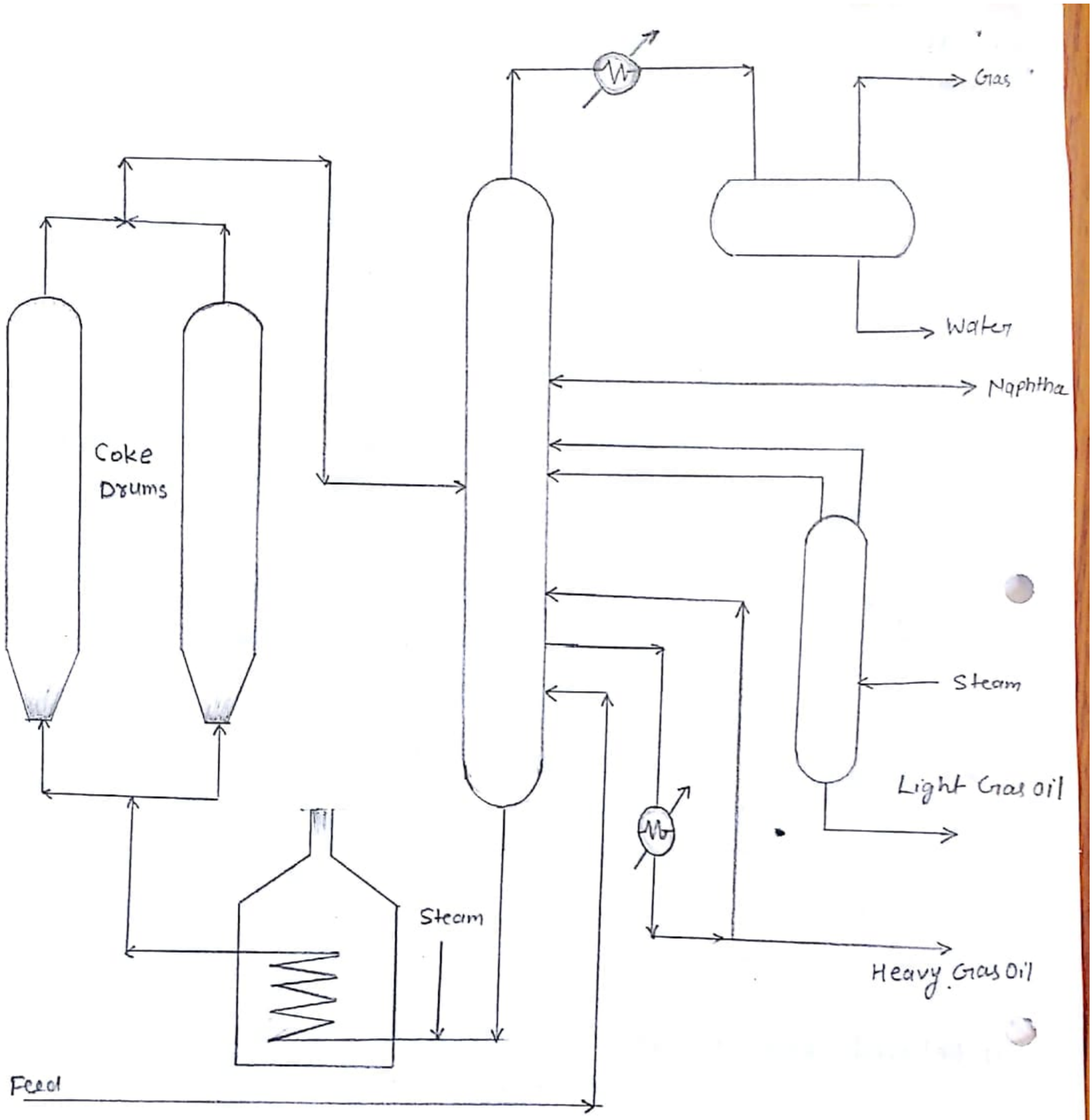


Fig: Flow sheet of Delayed Coking Process

ii)⇒ 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 over head vapour & coke thus formed is removed continuously. The fluid coker also has an additional scrubber which will remove heavier compounds from the vapour (if any) and send them back with the feed stream. Here the feed stream absorbs heavier hydrocarbons from the vapours generated. This is required as it is difficult to keep heavier hydrocarbones in the feed phase only due to pertinent high temp. The coke after coking reaction is cold coke. Therefore, to generate hot coke, a burner unit is used to heat the coke using exothermic CO_2 reaction. The offgases from the burner are sent to cyclones scrubbing and then to the vent. The hot coke thus obtained is recycled

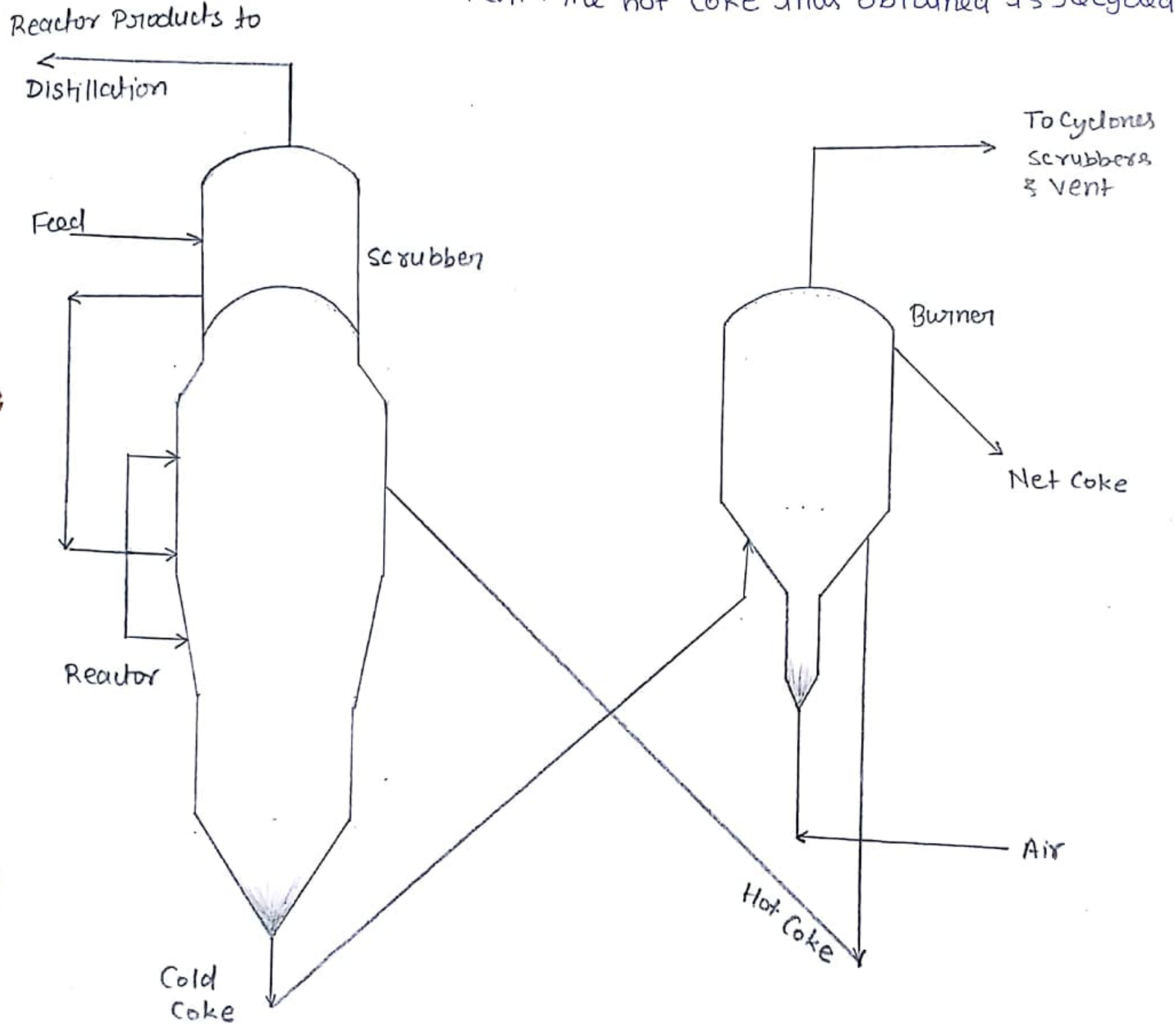


Fig: Flow Sheet of Fluid Coking Process

back to the fluidization 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 & heavy gas oil are obtained.
- Additional complexities in the distillation unit are.

i). Feed entering the distillation column but not the coker unit: This is to facilitate the removal of light ends from the feed (if any) & do not subject them to cracking. This is also due to the reason that light ends.

are valueable commodities and we donot want to the reason loose them to produce cheap coke product. In this case, the bottom product from the distillation column is feed to the furnace for pre-heating & subsequent coking operation.

ii). Live steam in distillation: This is to facilitate easy removal of lighter hydrocarbones in various sections.

iii). 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 issue, pleasure refer to the crude distillation process.