

PETROLEUM INDUSTRY

Chemical Process Technology

CHE F419

PETROLEUM INDUSTRY

- The **petroleum industry** includes the global processes of [exploration](#), [extraction](#), [refining](#), transporting (often by [oil tankers](#) and [pipelines](#)), and marketing [petroleum products](#).
- The largest volume products of the industry are [fuel oil](#) and [gasoline](#) (petrol). Petroleum is also the raw material for many [chemical products](#), including pharmaceuticals, solvents, fertilizers, pesticides, and plastics.

Crude Oil

- Crude oil is a complex mixture consisting of more than 10^8 compounds (gaseous, liquid and solid hydrocarbons, occurring in sedimentary rock) .
- 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.
- Elemental composition of crude oil :

Element	C	H	N	O	S
Percentage renage (wt%)	80-87	10-14	0.2-3	0.05-1.5	0.05-6

- The larger part of crude consists of alkanes (both linear and branched), cycloalkanes, and aromatics.

Crude Chemistry

- Based on chemical analysis and existence of various functional groups, refinery crude can be broadly categorized into about 9 categories summarized as
 - 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.
 - 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. 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.
 - 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.

5. **Napthalenes:** Polynuclear aromatics such as naphthalenes consist of two or three or more aromatic rings. Their molecular weight is usually between 150 – 500.
6. **Organic sulphur/nitrogen 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. Ever growing environmental legislations indicate technology and process development/improvement on the processing of organic sulphur compounds.
7. **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.
8. **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.
9. **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.

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.
- 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. Followed by absorption, extraction, heat transfer, fluid flow.
- 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.

Crude Oil Cuts & Refinery 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

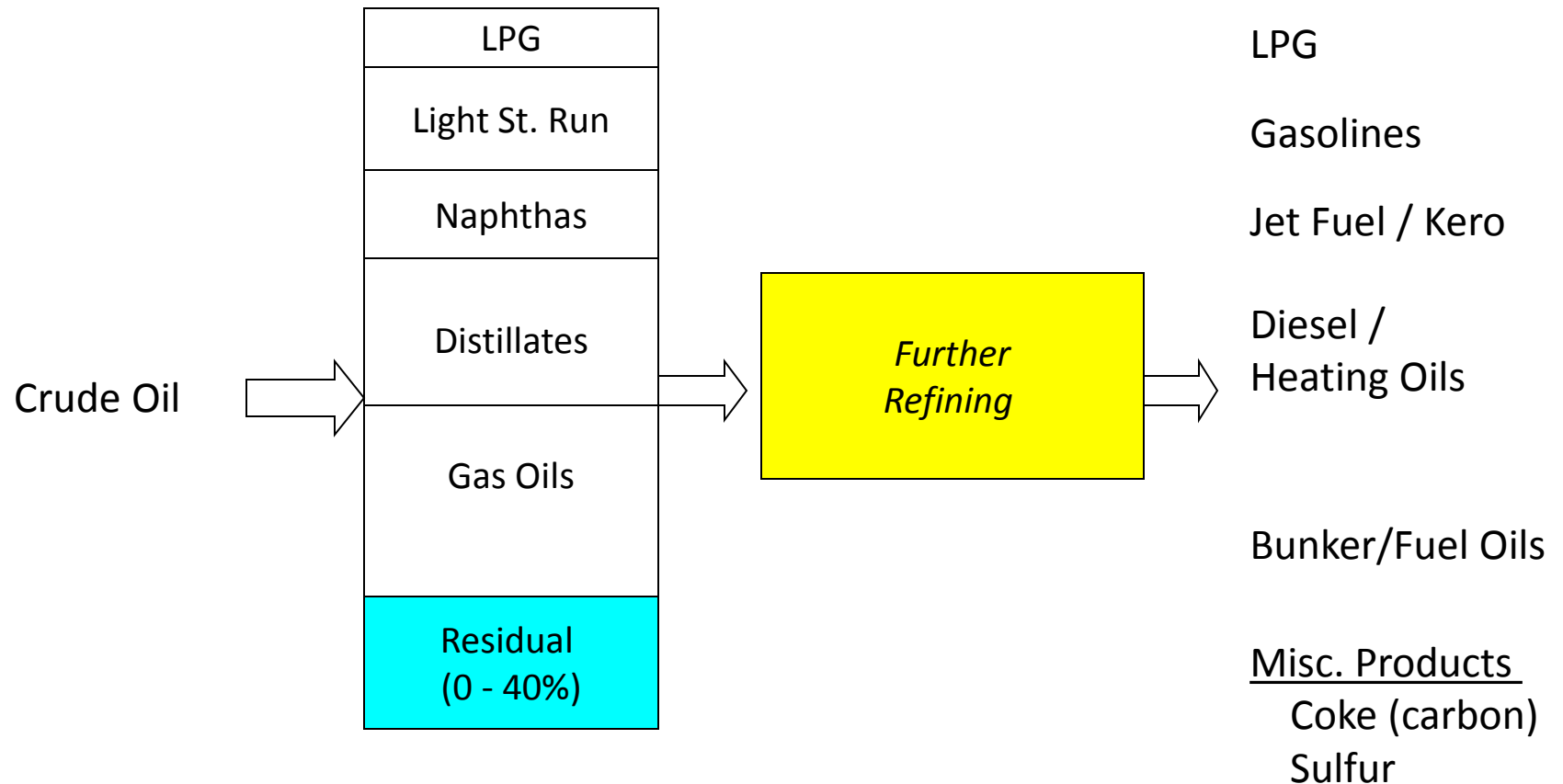
 - c. Coke

Petroleum Product	Composition	Uses
Liquefied petroleum gas (LPG)	Mixtures of saturated and unsaturated hydrocarbons (HCs) in C ₃ and C ₄ range.	Domestic fuel, Fuel for internal combustion engine and feedstock for many chemicals and olefins.
Naphthas	Light HCs boiling in the gasoline range. C ₅ : 60-85 °C , 85-110 °C 110-140°C (Up to C ₁₃)	Light – Gas making gasoline Intermediate- Aviation, Motor, Marine gasoline. Benzene, toluene, xylene. Olefins and diolefins.
Motor Spirit (Petrol or Gasoline)	Light distillate of boiling range 30-180°C, Consists of HCs ranging from C ₅ to C ₁₀ Straight chain paraffins (P), iso-P, cyclo-P, Aromatics.	Fuel for internal combustion engine
Kerosene	Distillate fraction in the boiling range 150-250°C. C ₁₀ to C ₁₄ paraffins, naphthanes, aromatic, non-HC compound (S,N,O and metals)	Domestic fuel : Cooking and lighting. Kerosene can not be burnt in the liquid state, it has to be first turned into vapor. Also used as insecticides, herbicides.
Aviation Turbine Fuel	Distillate fraction in the boiling range 150-270°C. Paraffins and naphthenes are major compounds.	Fuel for gas turbine engines.

Petroleum Product	Composition	Uses
Diesel Fuels	Less volatile middle distillate in boiling range 150-400°C. Contains paraffins, naphthanes, aromatic with carbon no. 12-18.	High speed diesel (HSD) for automobiles. Light diesel oil (LDO) for ship fuel
Fuel Oils	Made up of residues remaining from CDU/VDU C ₁₆ and above	Fuel Oils are used in industrial furnaces and boilers.
Lubricating Oils(2-4 % of total crude oil processed)	Carbon no. 16-20 or more, Containing aromatics, paraffins. Synthetic lubricants are synthesized using ethylene, acids, alcohols, esters.	Lubricating oil base stock, as lubricant in automobile engines Chemical additives
Petroleum Waxes	Hydrocarbon waxes consists of n and iso-paraffins, alkylated naphthenes in the range C ₁₈ -C ₇₀ .	Match Industry, candle manufacture, textile, paper waxing
Bitumens (Asphalts)	Viscous liquid or solid. Comprise range of products, exhibit thermoplastic behavior.	Water proofing properties, adhesives, Road applications.
Coke	Solid byproduct, Produced from coking	Carbon source (Electrodes), Fuel use.

REFINERY PRODUCTS

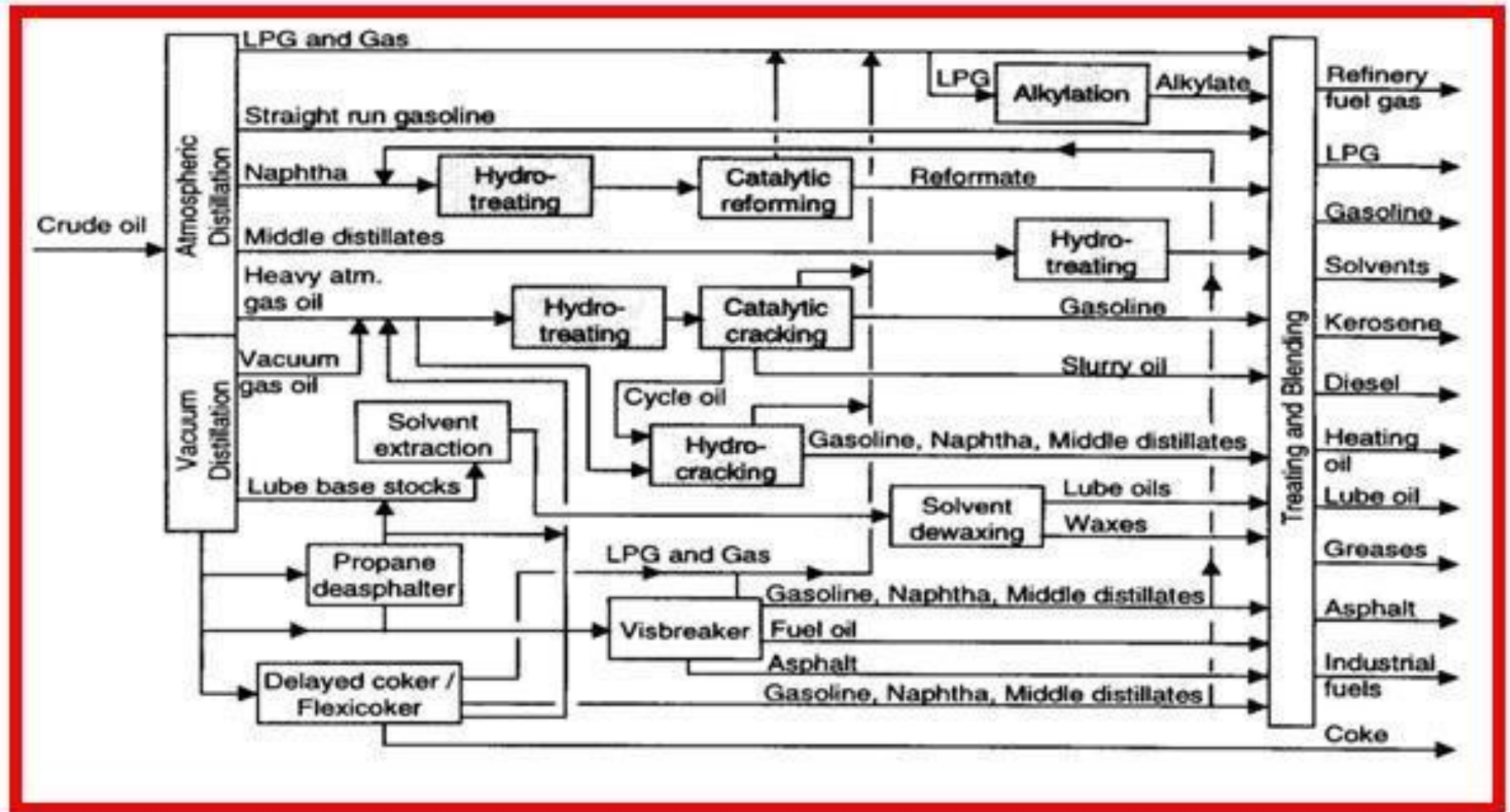
Crude Oil Distillation



Feed & 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.

Refinery Flow sheet



OIL REFINERY PROCESSES

- PHYSICAL PROCESSES
 - Desalting / Dehydration
 - Crude distillation (CDU & VDU)
 - Propane Deasphalting
 - Solvent Extraction
- THERMAL PROCESSES
 - Visbreaking
 - Delayed coking
- CATALYTIC PROCESSES
 - Catalytic Cracking
 - Hydrotreating
 - Hydrocracking
 - Catalytic Reforming
 - Alkylation
- CONVERSION OF HEAVY RESIDUE
 - Flexicoking

Physical Processes

- Desalting/Dehydration

Crude oil often contains water, inorganic salts, suspended solids and water-soluble trace metals. These contaminations cause corrosion, plugging and fouling of equipments and poisoning of catalyst in catalytic processes.

Desalting and dehydration is accomplished by adding hot water with added surfactant to extract the contaminants from the oil. Upon heating, the salt and other impurities dissolve into water or attach to it. The oil and water phase are then separated in a tank, where water phase settles out, the desalted crude is drawn from the top and sent to crude distillation column.

- ## Crude Distillation

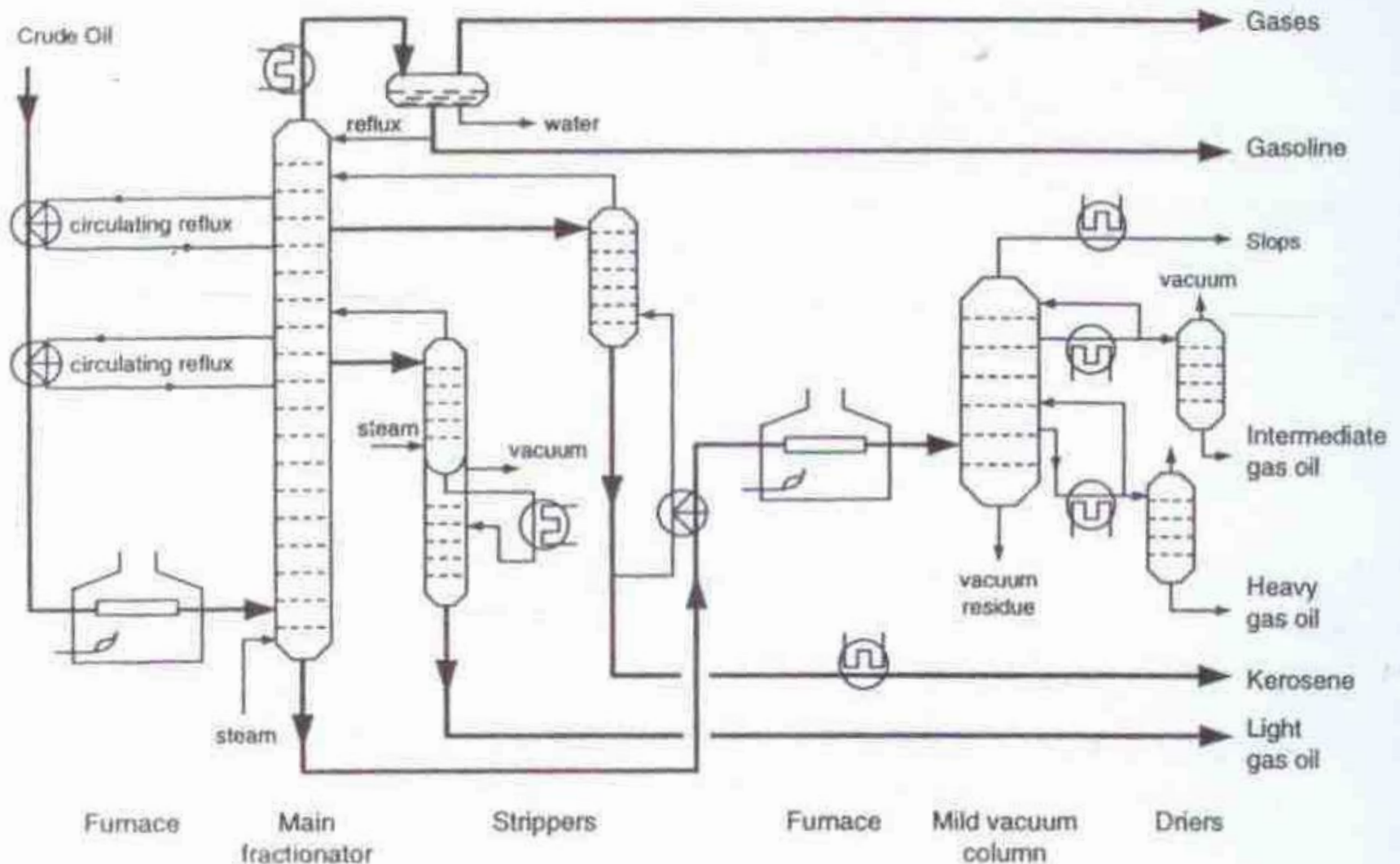
The central separation step in every oil refinery is distillation of crude, which separates the various fractions according to their volatility.

After heat exchange with residue the crude oil feed is heated further to about 620 K in a furnace, then charged to distillation tower. A distillation column typically is 4 m in diameter and 20-30 m in height and contains 15-30 trays. The stripping columns, which may be 3 m high with a diameter of 1 m, serve to remove the more volatile components from the side streams.

High temperature (above 630 K) is limitation of atmospheric distillation, since thermal decomposition take place above this temperature. Thermal decomposition (cracking/pyrolysis) is undesirable because it result in deposition of carbonaceous material on tube walls.

Thus vacuum distillation unit (VDU)is employed, to process atmospheric distillation residue, under reduced pressure (<0.1 bar). A vacuum column usually has a much larger diameter (up to 15 m) than the atmospheric column because of the large volumetric flow rate due to reduced vapor pressures.

Crude Distillation Unit (CDU) with Vacuum Distillation Unit (VDU)



- ## Propane Deasphalting

The coke-forming tendencies of heavier distillation (from atmospheric and vacuum residue) can be reduced by removal of 'asphaltenic' materials by means of extraction.

Process Variables :

Extraction T : Top (75-85 °C) Bottom (50-65 °C)

Pressure: 3.5 -4 MPa

Liquid propane, butane and pentane are suitable solvents.

Deasphalting is based on the solubility of hydrocarbons in solvent.

Heavy feed and solvent are contacted counter currently. Alkanes present in feed dissolve in the propane, whereas the asphaltenic material (aromatic compounds), the coke 'precursors' do not dissolve.

Propane evaporates on depressurization and is condensed and recycled.

The asphalt residue is then sent to thermal processes like 'Flexicoking', 'Delayed coking' and 'visbreaking'

- **Solvent Extraction**

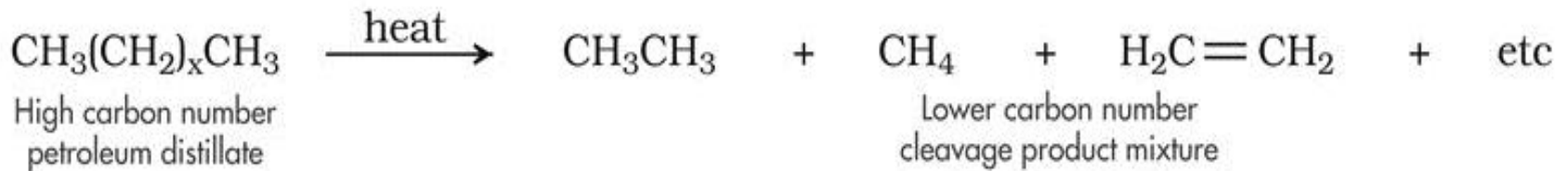
It is widely used method to remove aromatics and other undesirable constituents from lube oil fractions.

It improves thermal-oxidation stability, viscosity index of lube oil base stock.

The most common solvents used are furfural, phenol and N-methyl-2-pyrrolidone (NMP).

Thermal Processes

When heating a hydrocarbon at higher temperature, thermal cracking takes place. This is referred to as 'pyrolysis'. Disadvantage is that large amount of low value products are formed. This is reason for innovations like flexicoking and processes optimized towards the production of certain types of high quality coke.



- **Visbreaking**

Visbreaking is relatively mild thermal cracking process in which the viscosity of vacuum residue is reduced.

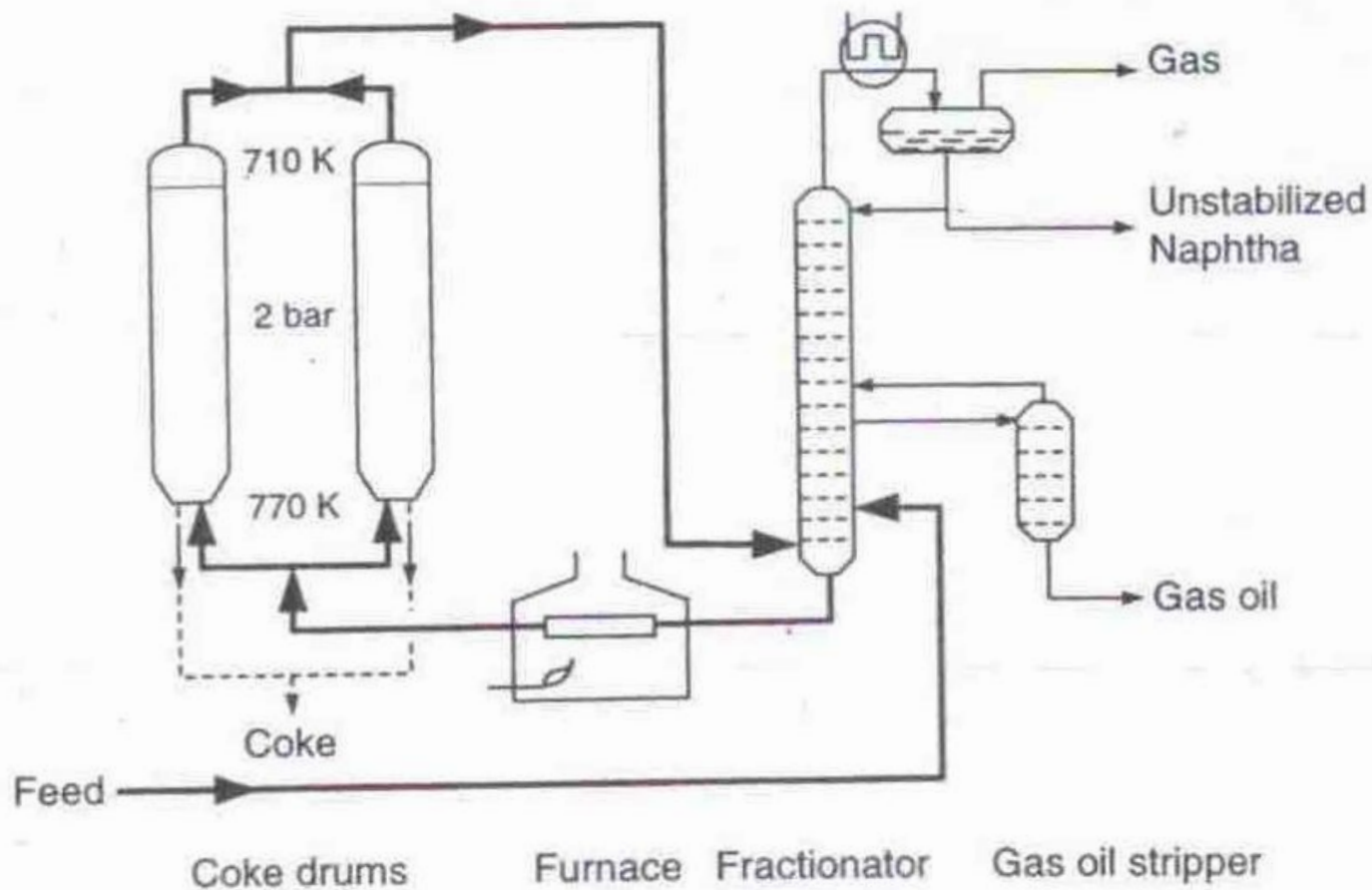
Temperature (710-760 K), Pressure 20 bar and reaction time (1-8 min).

Usually less than 10% by weight of gasoline and lighter products are produced. The main product is cracked residue with lower viscosity.

- Delayed Coking

Delayed coking is a thermal cracking process with long residence times, forming solid residue (coke) also.

Produced coke with desired properties (e.g. coke for electrodes)



Catalytic Processes

Most important catalytic processes in the oil refinery are

- Fluid catalytic cracking (FCC)
- Hydro-treating
- Hydro cracking
- Catalytic Reforming
- Alkylation

The high demand of diesel (linear alkanes: high cetane no.) and gasoline (branched alkanes, aromatics: high octane no.) results in additional conversion steps such as catalytic cracking and hydrocracking, which converts heavy hydrocarbons into lighter ones.

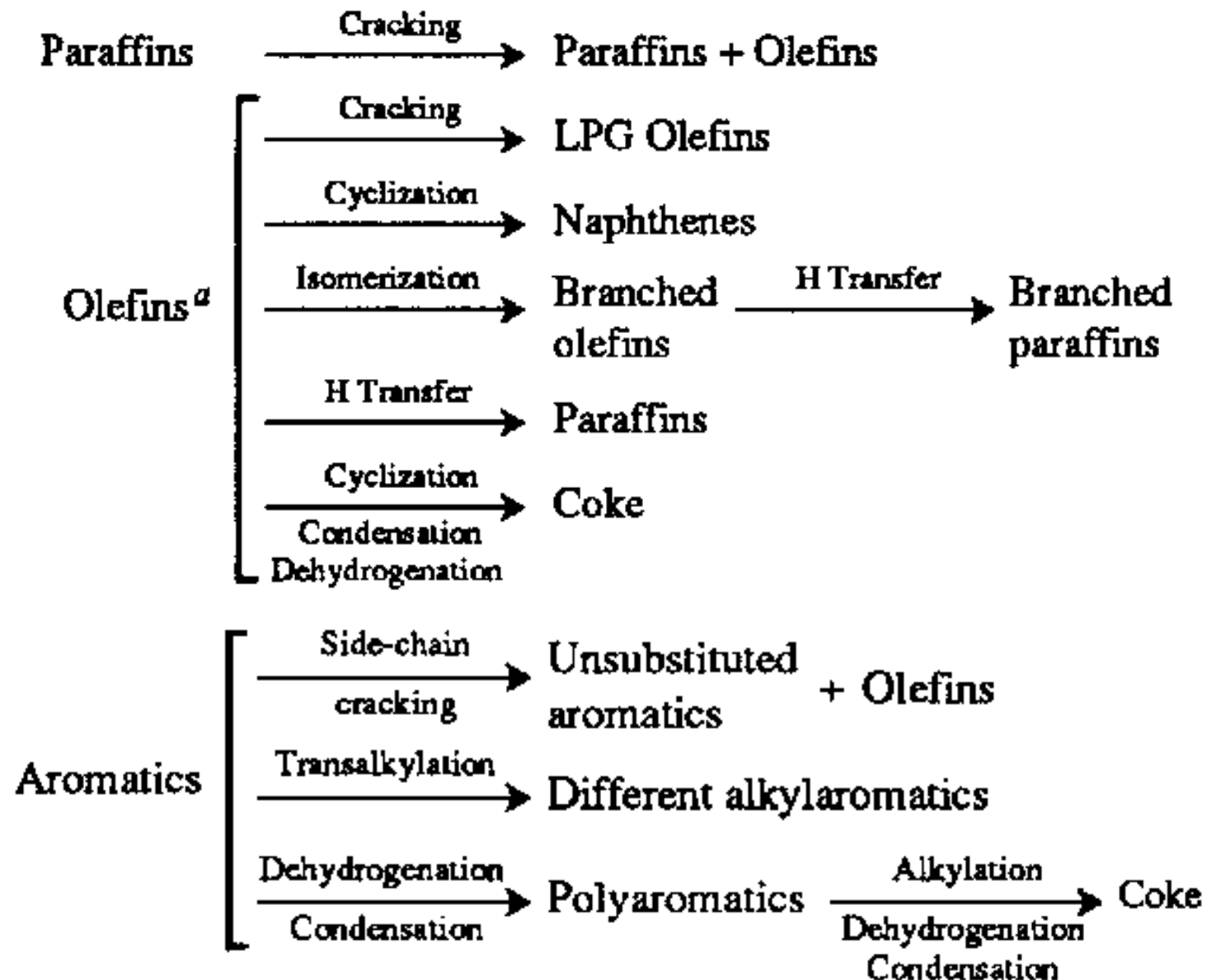
Catalytic reforming, re-forms gasoline range HCs into higher octane number HCs.

Alkylation, combines lower alkenes with isobutane to form high octane gasoline components

• Catalytic Cracking

- The main incentive of catalytic cracking (endothermic reaction) is the need to increase gasoline production.
- Feedstocks are heavy oil fractions, vacuum gas oil.
- Cracking is catalyzed by solid acids, which rupture C-C bonds. In thermal cracking, bond rupture is random, while in catalytic cracking it is ordered and selective.
- There are many pathways leading to coke formation (reactions shown on next page). The formed coke deposit on the catalyst, thus causes deactivation. So regeneration of catalyst is necessary.
- Regeneration is carried out by combustion in air at 973 K. This is highly exothermic reaction, which provides necessary energy for the endothermic cracking operation.
- Originally, fixed bed and moving bed reactors were applied, but nowadays FCC is predominant process.

Main Reactions in FCC Catalysis



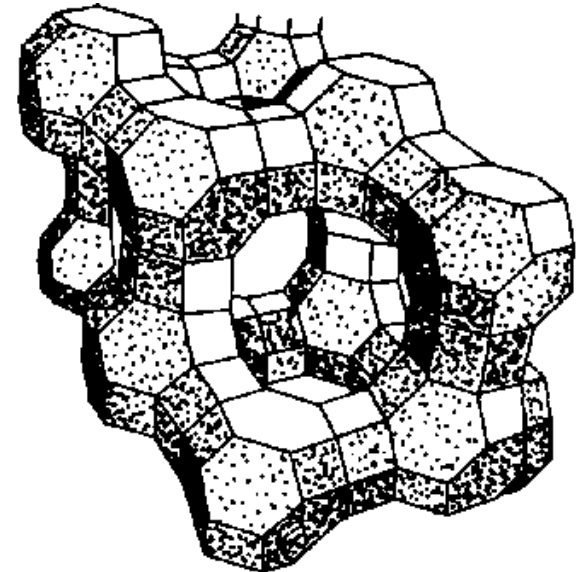
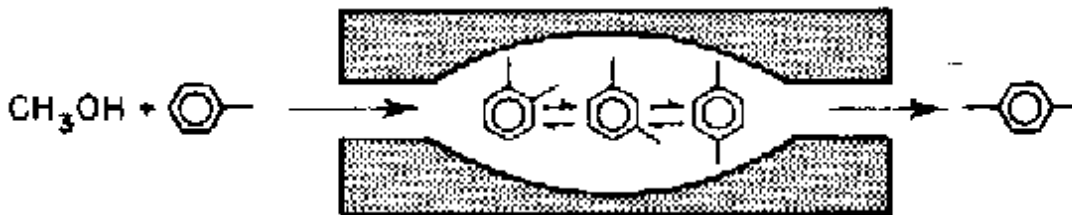
FCC Catalyst development

- Catalytic cracking require acid catalyst.
- Initially AlCl_3 solutions and acid-treated clays were used.
- Later, synthetic material viz. amorphous silica-alumina were found with higher thermal and attrition stability, higher activity and optimal pore size.
- Further, better catalyst zeolites are discovered with more activity and stability (less coke, higher thermal stability).
- With current zeolite catalyst much less gas oil needs to be processed in an FCC unit than with amorphous catalyst.

- Zeolites are three-dimensional structures constructed of SiO_4 and AlO_4 which are joining by sharing the oxygen ions.

- Zeolite contains very well defined strong acid sites. Due to there very high activity, the zeolite particles are diluted with a macro/meso-porous material (silica-alumina).

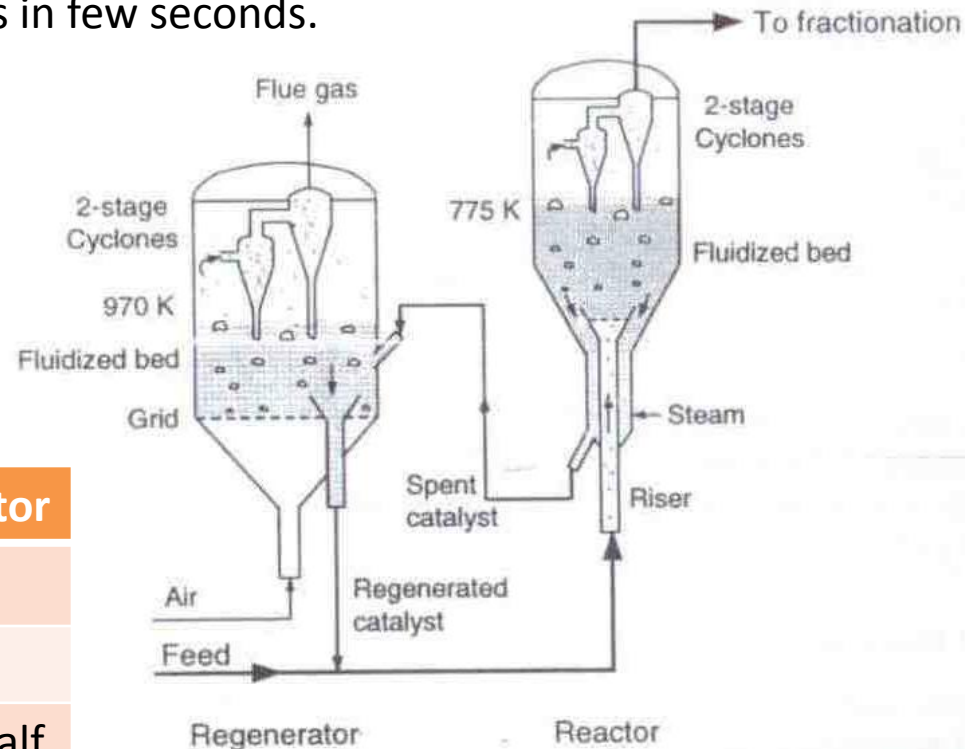
- Product Selectivity is shown in figure below:



FCC Process description

- In reactor heat is consumed by the cracking reactions, while in the regeneration unit, heat is produced.
- The catalyst is circulated continuously between the two fluidized bed reactors and act as vehicle to transport heat from regenerator to the reactor.
- Riser is employed to approximate plug flow.
- The cracker feed is diluted with steam for better atomization, and fed to the riser reactor together with regenerated catalyst.
- The mixture flow upwards and cracking takes in few seconds.
- The spent catalyst is separated from the reaction mixture in a cyclone.
- The catalyst is transported to a fluidized-bed regenerator where coke is removed from the catalyst by combustion with air.
- Typical operating conditions in riser FCC are given in table below:



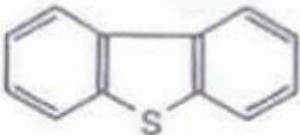
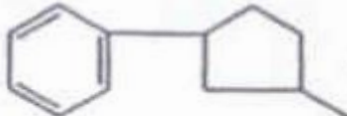
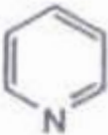

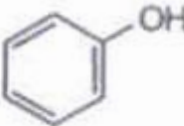

	Reactor	Regenerator
Temperature [K]	775	973
Pressure (bar)	1	2
Residence time	1-5 s	Minute/half hour



• Hydrotreating

- Belongs to the conversions involving reaction(exothermic) with hydrogen.
- It involves both hydrogenolysis and hydrogenation reactions
 - Hydrogenation : Addition of hydrogen to double bonds, triple bonds, aromatic rings takes place.
 - Hydrogenolysis : Involves breaking of C-S, C-N bonds.
- In contrast to 'hydrocracking' in which size reduction is the main objective, in hydrotreating molecular size is not drastically altered.
- The major objectives of hydrotreating are protection of downstream catalysts (hetero-compounds often act as poison), improvement of gasoline properties (odor, color, stability, corrosion) and protection of environment.
- In naphtha reforming, hydrotreating is applied as a pre-treatment step to protect Pt-catalyst against S-poisoning.
- The hydrogen used in naphtha hydrotreating is a by-product of catalytic reforming. Whereas hydrotreating of heavy residue require separate hydrogen production unit.
- Most hydrotreating of heavy feedstock is performed in trickle bed reactor.
- **Temperature** : 600-670 K; **Pressure** : 15-40 bar (Naphtha) 40-100 bar (Gas oil)
- **Catalyst** : Mixed metal sulfides (CoMoS/ CoS/NiS/MoS₂) on Al₂O₃

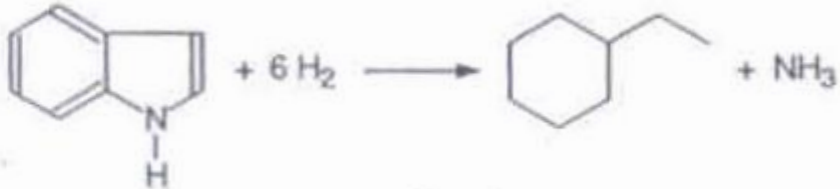
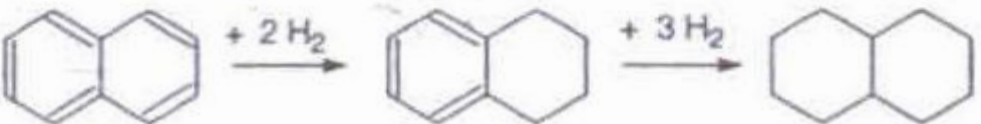



Hydrotreating Reactions

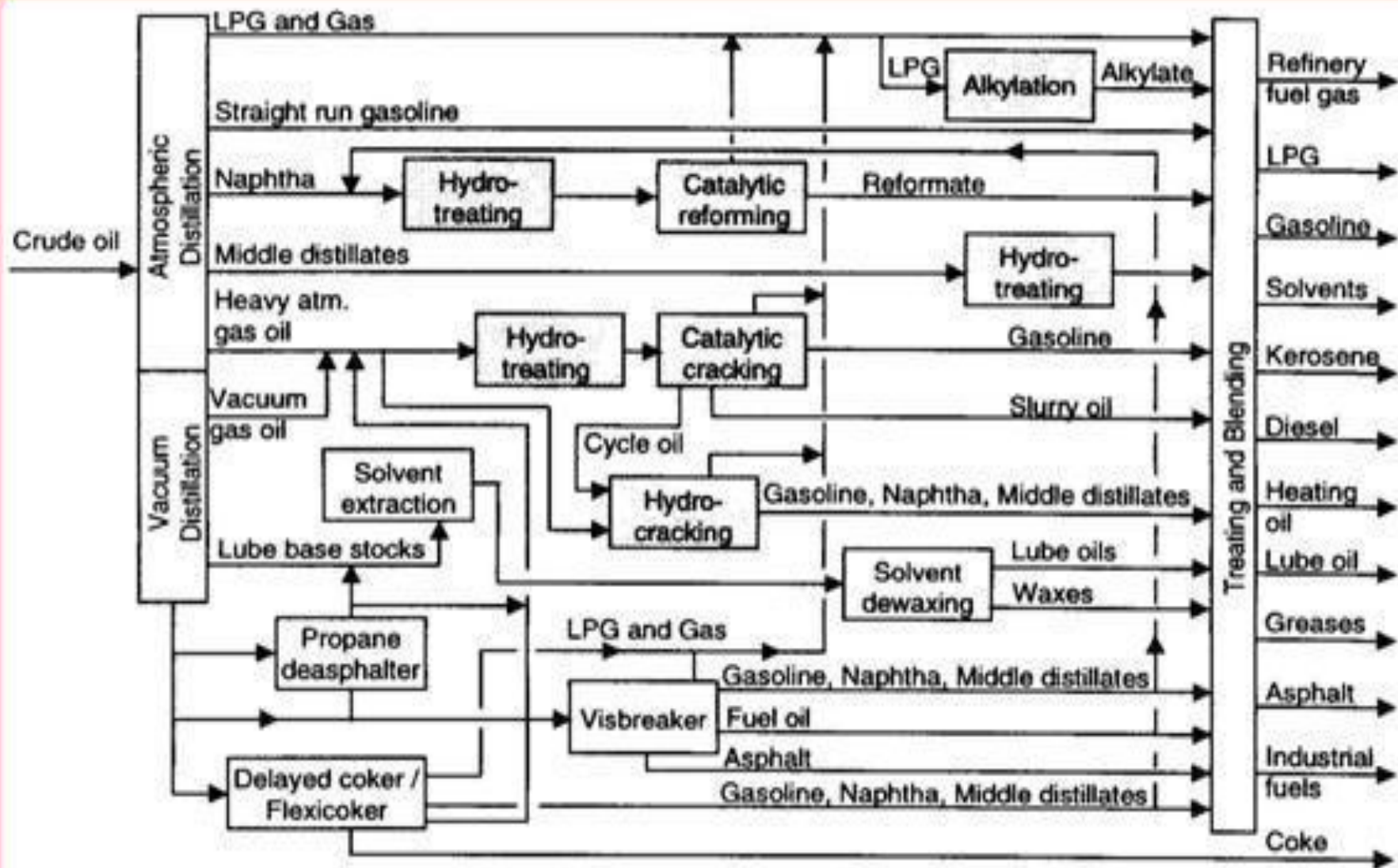
Compound	Example		ΔH_{298}^0 (kJ/mol)
Mercaptans	RSH	$+ \text{H}_2 \longrightarrow \text{RH} + \text{H}_2\text{S}$	- 72*
Thiophenes		$+ 3 \text{H}_2 \longrightarrow$  $+ \text{H}_2\text{S}$	- 147
Benzothiophenes		$+ 5 \text{H}_2 \longrightarrow$  $+ \text{H}_2\text{S}$	- 225
Pyridines		$+ 5 \text{H}_2 \longrightarrow$  $+ \text{NH}_3$	- 333
Phenols		$+ \text{H}_2 \longrightarrow$  $+ \text{H}_2\text{O}$	- 62

- **Hydrocracking**

- Hydrocracking involves the cracking of relatively heavy oil fraction into lighter products (naphtha, diesel oil, kerosene) in presence of hydrogen.
- This distinguishes the process from the FCC process, which does not have hydrogen in the feed, and from hydrotreating process in which no C-C bond breaking takes place.
- The catalytic cracker takes the more easily cracked alkane-rich atmospheric and vacuum gas oils as feedstocks, while the hydrocracker uses more aromatic feeds, such as FCC cycle oils and distillate from thermal cracking processes.
- Various process configurations have been developed
 - Single stage, Two stage, Series flow hydrocracking
- Temperature: 610-710 (single stage), 530-650 (Second stage)
- Pressure : 100-150 bar
- Catalyst : Ni/Mo/S/Al₂O₃ +P; Ni/W/S/Zeolite

• Hydrocracking Reactions

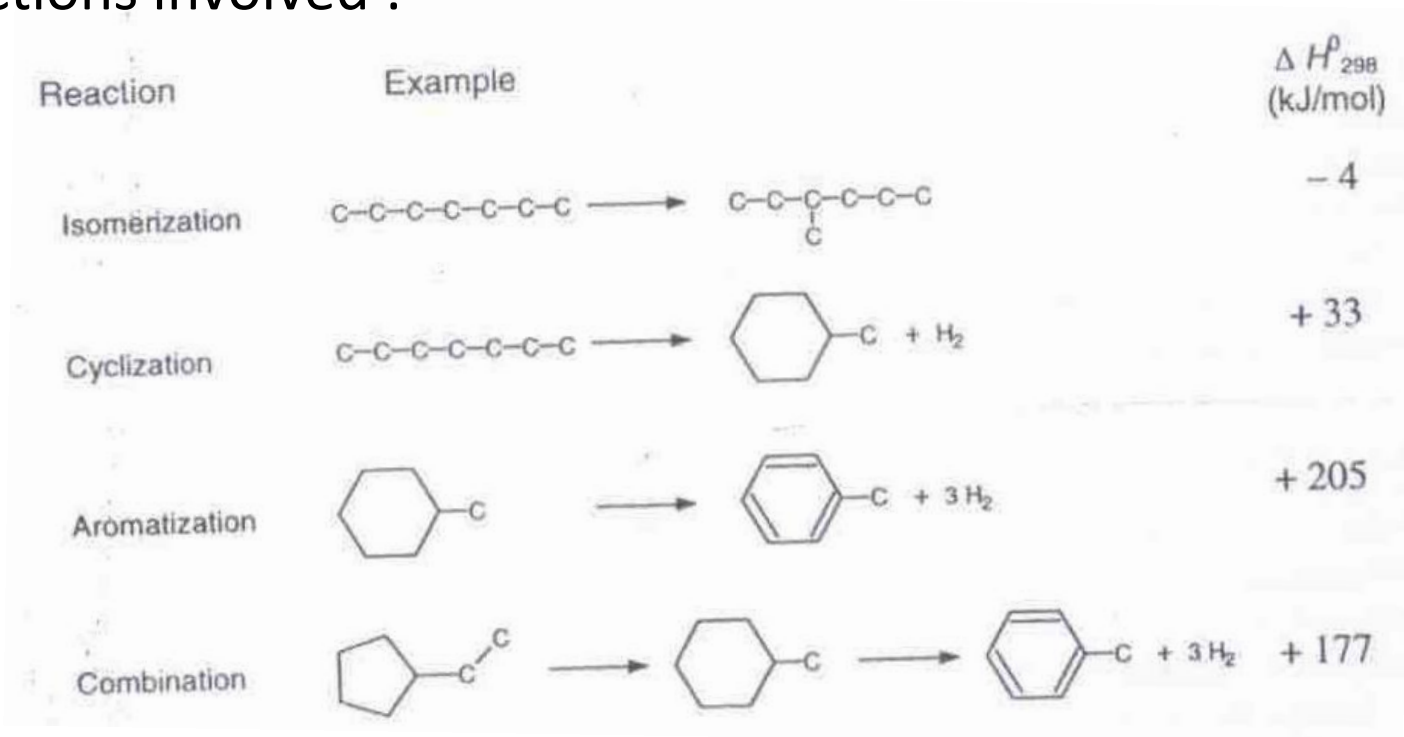
Reaction	Example	ΔH_{298}° (kJ/mol)
Hetero-atom removal		- 374
Aromatics hydrogenation		- 326
Hydrodecyclization		- 119
Alkanes hydrocracking		- 44
Hydro-isomerization		- 4



• Catalytic Reforming

- Catalytic reforming is used to convert hydrocarbon to aromatics which have high octane number (eg –Benzene, toluene). These aromatics are also important feedstock for chemical industry.
- Furthermore Catalytic reforming is major source of oxygen
- Feedstocks are straight run Naphtha and other feeds in gasoline boiling range (about C₆-C₁₁).

• Reactions involved :



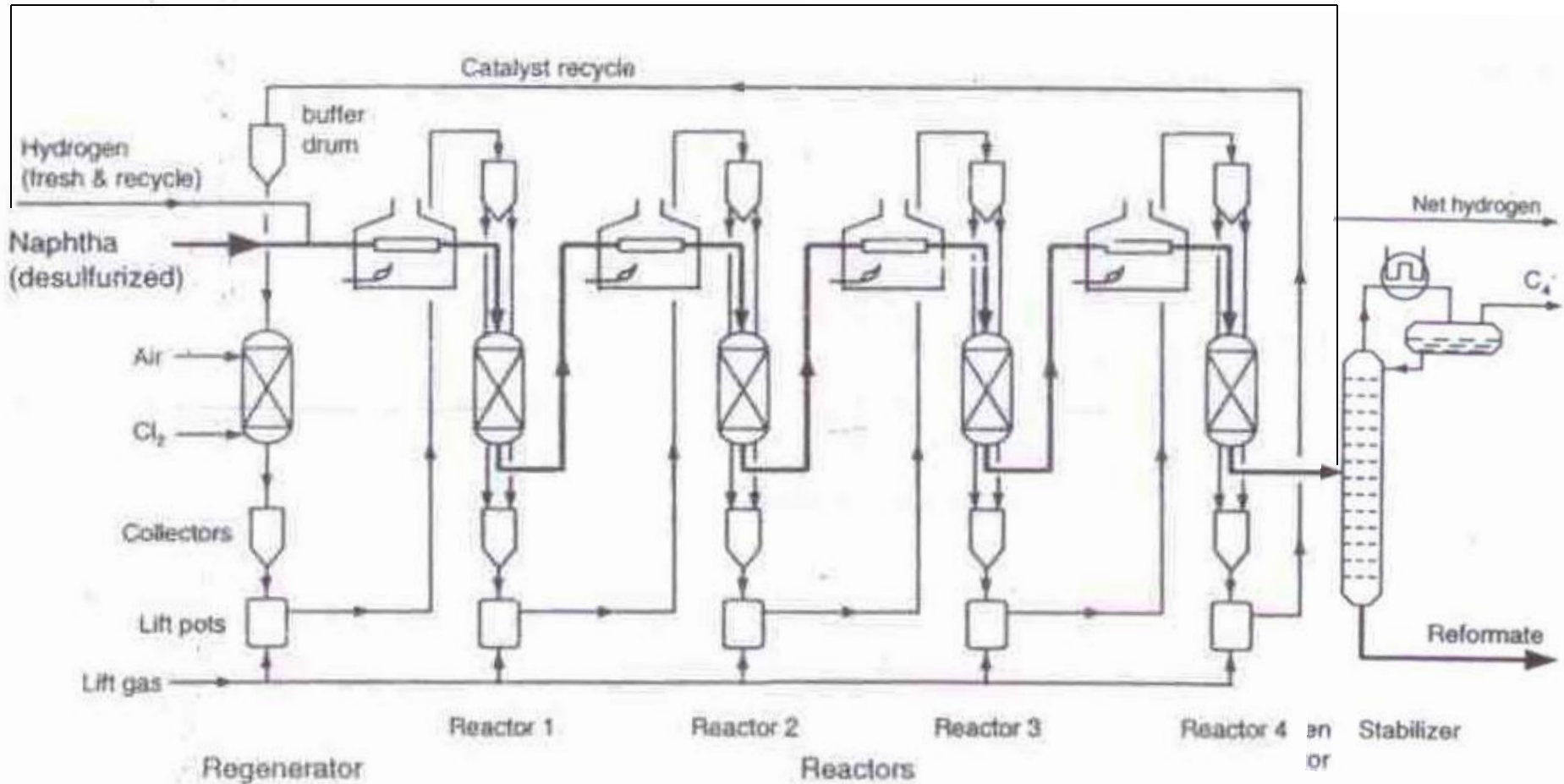
- Catalyst :

- Platinum, molybdenum oxide, chromium oxide, cobalt molybdate, alumina or silica alumina base.
- The dehydrogenation and aromatization reactions are catalyzed by metal catalysts. The isomerization and cracking reactions require an acidic catalyst.
- In catalytic reforming, the catalyst consists of platinum metal (that's why the name PLATEFORMING is also often used), dispersed on alumina. The alumina support has some acidity, which enhance by adding chlorine.
- Feed treatment (by hydrotreating) is required as Pt is sensitive to deactivation by hydrogen sulfide, ammonia and other S,N compounds.

- Reforming Processes :

- Two main type of processes applied in catalytic reforming
 - Semi-regenerative reforming (SRR) [15-20 bar] : Fixed bed
 - Continuously-regenerative reforming (CRR) [3-4 bar] : Moving bed

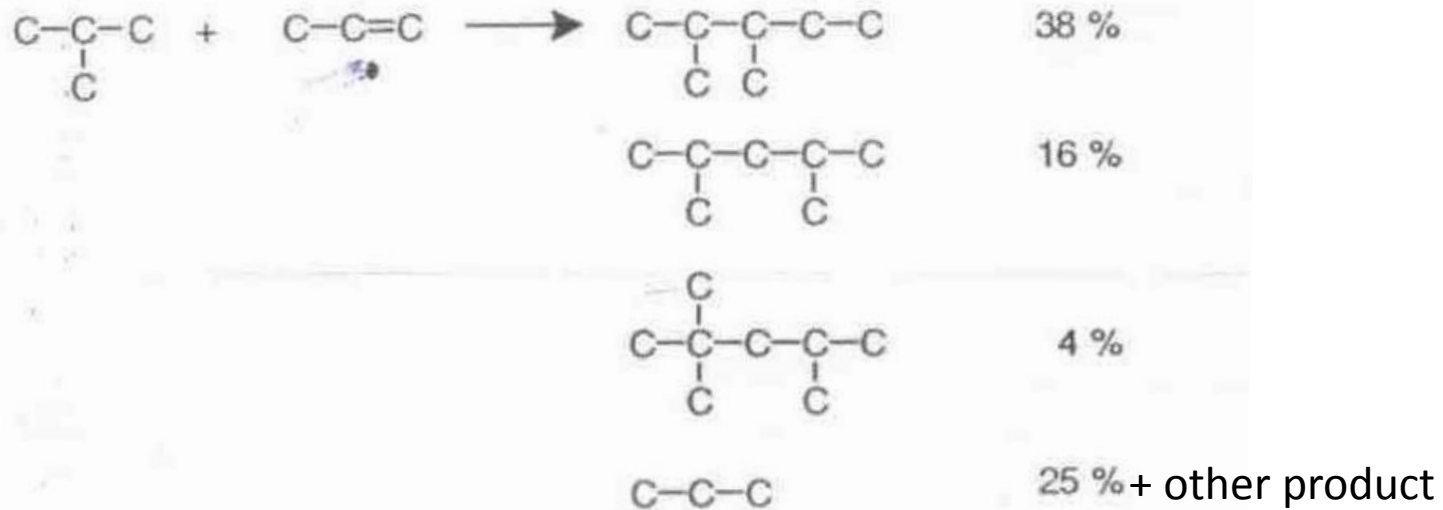
Process flow sheet (CRR)



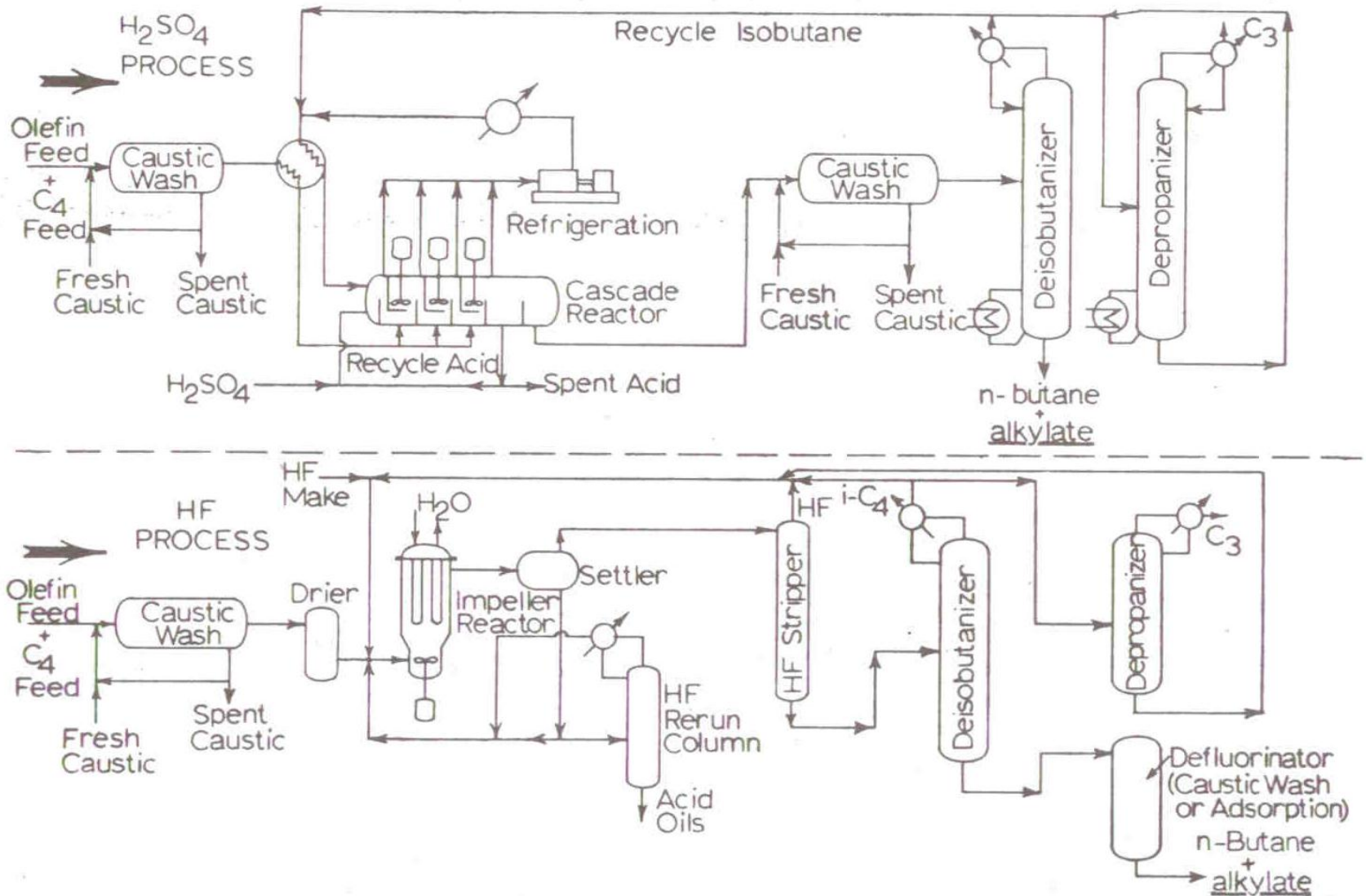
Alkylation

- Alkylation is the reaction of alkenes with isobutane to form higher branched alkanes, alkylate (gasoline range).
- The aim is the production of high octane number gasoline component from low molecular weight alkenes (propene, butenes, and pentenes).
- Catalytic process (<340 K, 2-20 bar) is applied, using H_2SO_4 or HF as catalyst.
- Reactions are exothermic in nature, best yield at low temperatures [H_2SO_4 catalyst more sensitive with 0°C lower limit due to viscosity effect and 21°C upper limit due to sulfation reaction].
- Excess iso-butane (8-12 times alkene e.g. propene) is fed to push reaction forward and to minimize polymerization of propene.

Reactions:



Alkylation Process Flow sheet



• Process Comparison

- A major problem with H_2SO_4 alkylation process is the consumption of acid (about 100 kg/t of product). The HF process is more favorable in this respect (1/10 of weight of H_2SO_4).
- The two process schemes are comparable. Most important difference is HF stripper is required for HF process.
- Another advantage of the HF alkylation process is reaction can be carried out at 310 K, which eliminates need for cryogenic cooling (refrigeration).
- Both HF and H_2SO_4 catalyzed processes suffer disadvantage such as pollution, safety and corrosion problems. Of the two sulfuric acid is safer as it stay in liquid form, so a leak of sulfuric acid is much more contained than hydrofluoric acid, which is highly volatile and toxic at ambient conditions. That's why sulfuric acid process dominates.

Novel development : Solid catalyzed alkylation

Other Refinery Processes

- Isomerization
- Conversion of heavy residue : Flexicoking
- Treatment of refinery gas streams
- Current & Future trends in Oil Refining
 - Reformulated Gasoline (FCC, isomerization, reforming)
 - Diesel (hydrocracking)
 - Solid acid catalyst

ISOMERISATION

- Definition: Isomerisation of n paraffin to isomers for alkylation feedstock is a necessary refinery operation since n paraffin are of little value.
- Reactions : Mildly exothermic
- Catalyst : Aluminum trichloride -HCl promoted adsorbed on porous carriers or used as liquids .
- Reaction conditions:
Temperature – 100-150 °C with 40-50% conversion
Pressure – no effect on reaction, 17 – 27 atms
Space velocity – 0.5 – 2.5 m³ hr m³ catalyst

ISOMERISATION

