CHAPTER 3

OIL REFINERY PROCESSES

OUTLINE

1. Introduction
2. Physical Processes
3. Thermal Processes
4. Catalytic Processes
5. Conversion of Heavy Residues
6. Treatment of Refinery Gas Streams

INTRODUCTION

- Oil refining is a key activity in the Chemical Process Industries.
- Over 600 refineries worldwide have a total annual capacity of more than 3500 x 10^6 tones.
- Goal of oil refining is twofold:

i. Production of fuels for transportation, power generation and heating

ii. Production of raw materials for the CPI.

Crude Oil

Crude oil is a non-uniform material.
The composition depends on its location.
Figure 2.11 shows the ratio of C/H in some of chemical compounds

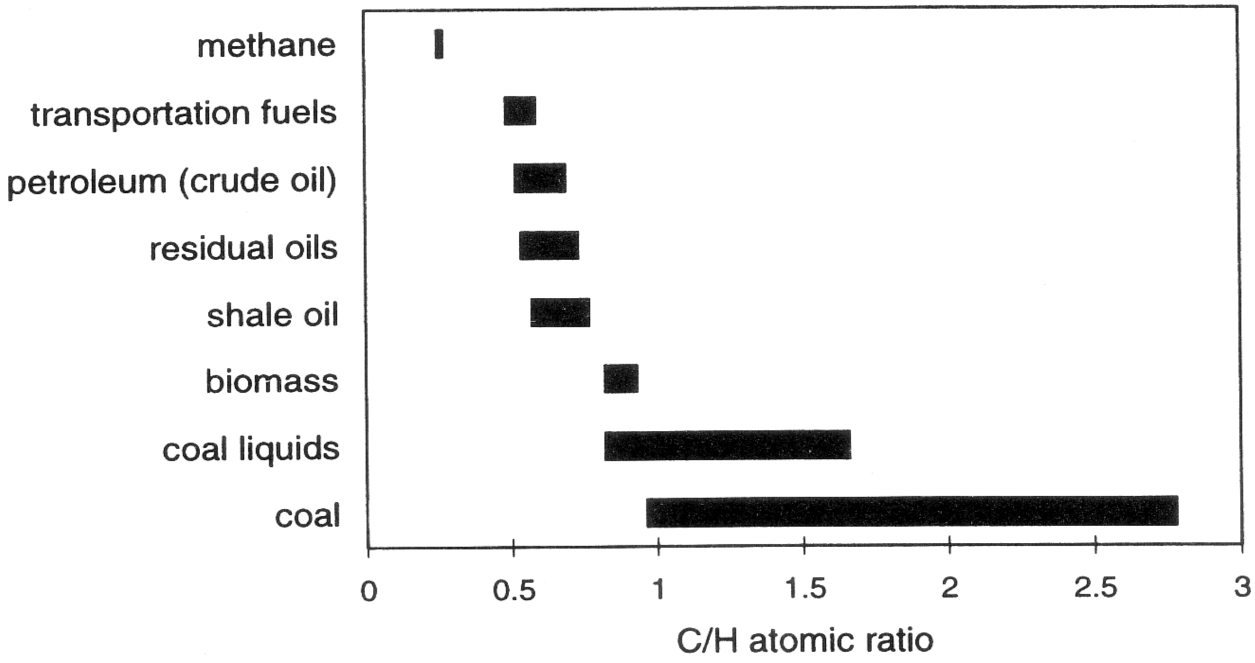


Figure 2.11 C/H atomic ratios of hydrocarbon sources and some products.

The majority of crude oil is alkanes, cycloalkanes (naphthenes), aromatics, polycyclic aromatics, Sulfur - containing compounds, etc.

Example: Gasoline: branched alkanes

Diesel: linear alkanes

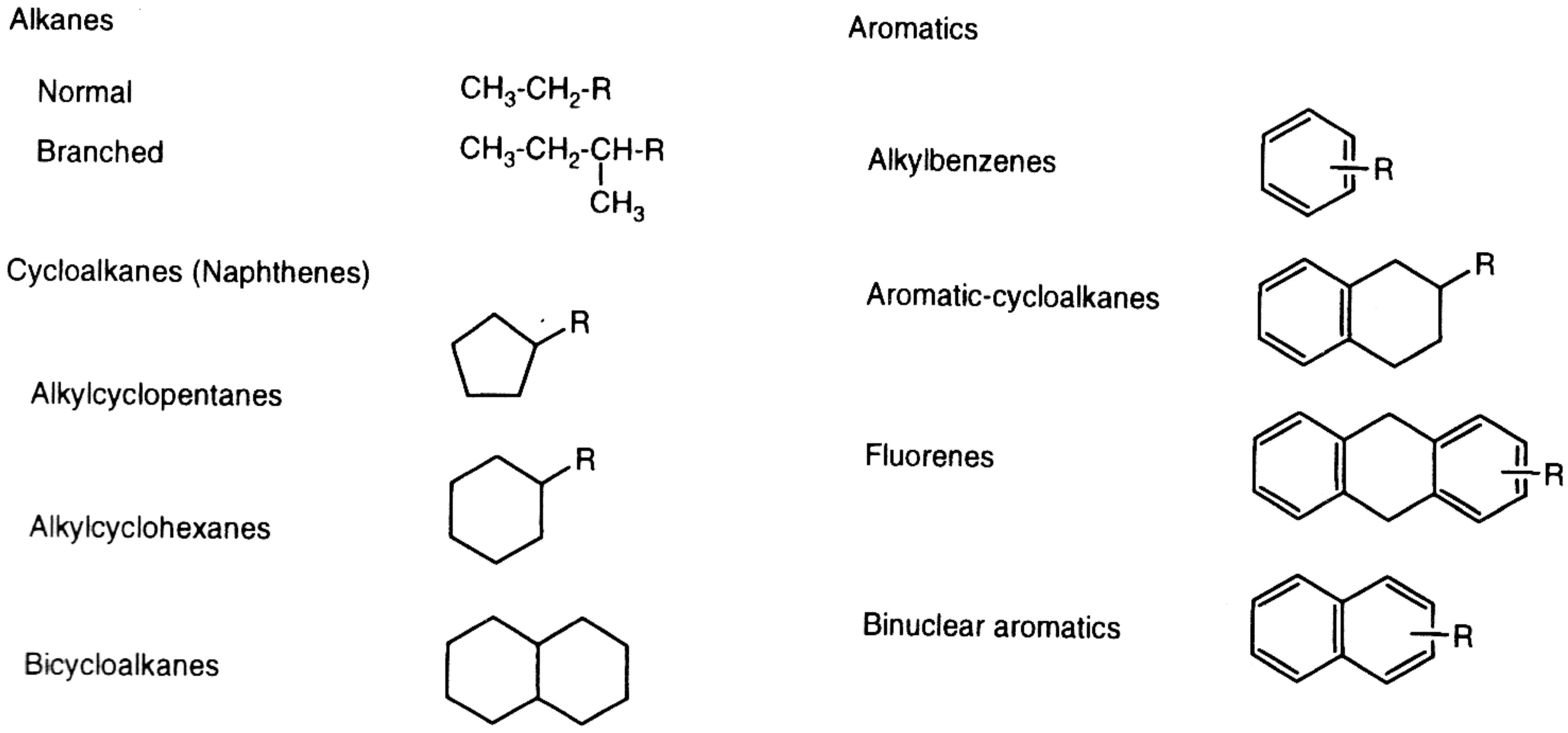


Figure 2.12 Examples of alkanes, cycloalkanes and aromatics present in crude oil.

Heavier crude contains more polycyclic aromatics lead to carboneceous deposits called “coke”

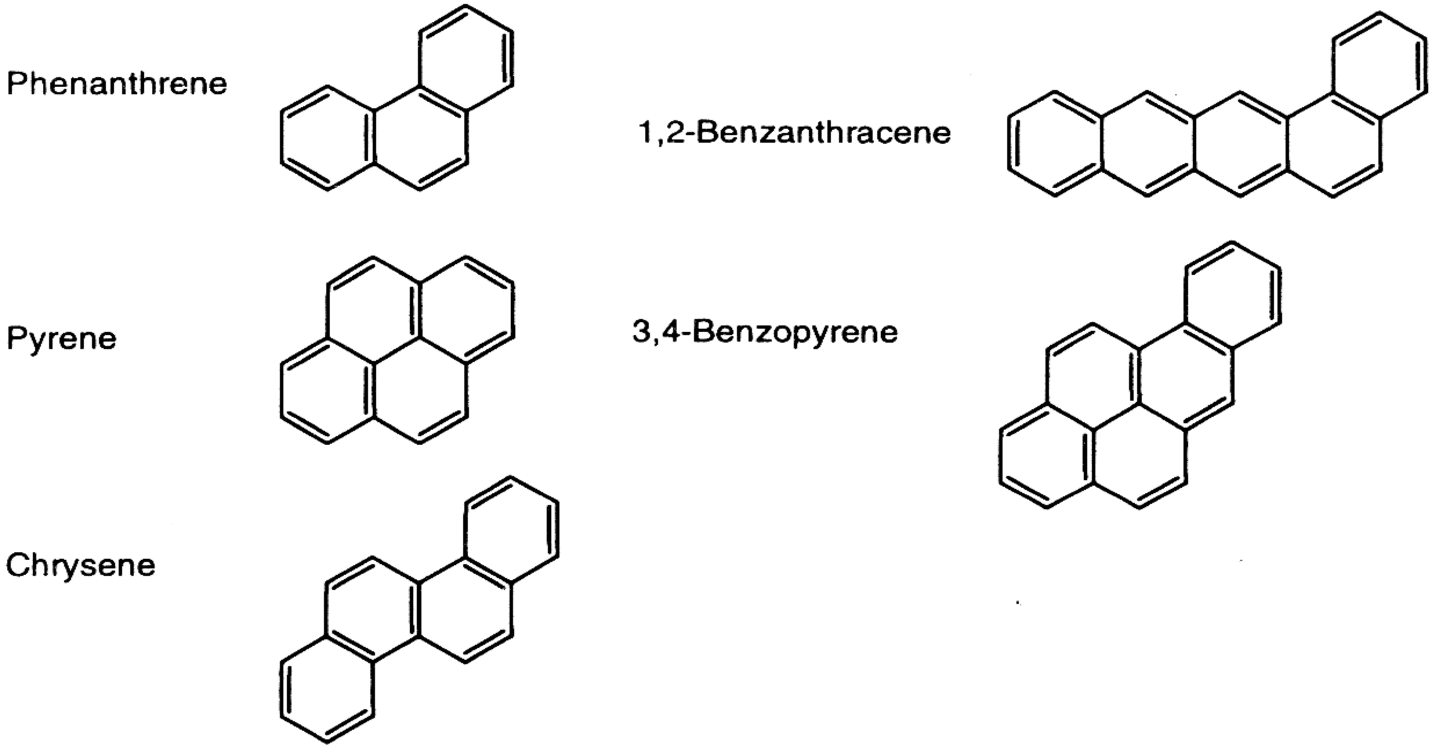


Figure 2.13 Examples of polycyclic, polynuclear aromatics in crude oil.

Some crudes contain a lot of sulfur, which leads to additional processing considerations.

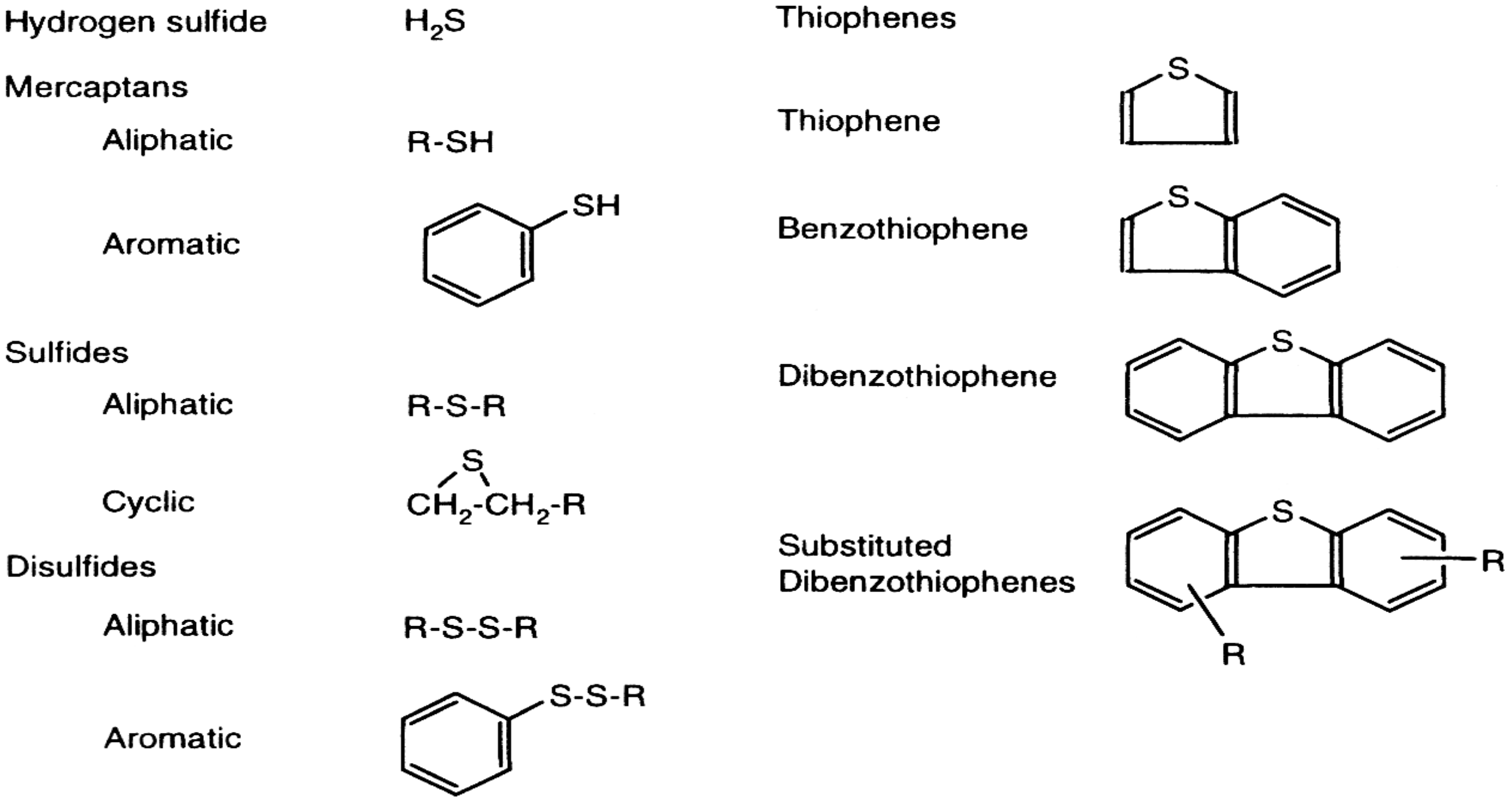


Figure 2.14 The most important sulfur-containing hydrocarbons in crude oil.

Overview

- After desalting and dehydration, crude is separated into fractions by distillation.
- The distilled fractions can not be used directly.
- The reason for such a complex set of processes is

1- the difference between the crude oil properties and the needs of the market.

2- environmental legislation demands cleaner products

3- is the major drive for process improvement and development of novel processes.

Refining operations

Petroleum refining processes and operations can be separated into five basic areas:

1. **Fractionation** (distillation) is the separation of crude oil in atmospheric and vacuum distillation towers into groups of hydrocarbon compounds of differing boiling-point ranges called "fractions" or "cuts."
2. **Conversion Processes** change the size and/or structure of hydrocarbon molecules. These processes include: **:**
   - Decomposition (dividing) by thermal and catalytic cracking;
   - Unification (combining) through alkylation and polymerization; and
   - Alteration (rearranging) with isomerization and catalytic reforming.
3. **Treatment Processes** to prepare hydrocarbon streams for additional processing and to prepare finished products. Treatment may include removal or separation of aromatics and naphthenes, impurities and undesirable contaminants. Treatment may involve chemical or physical separation *e.g.* dissolving, absorption, or precipitation using a variety and combination of processes including desalting, drying, hydrodesulfurizing, solvent refining, sweetening, solvent extraction, and solvent dewaxing.

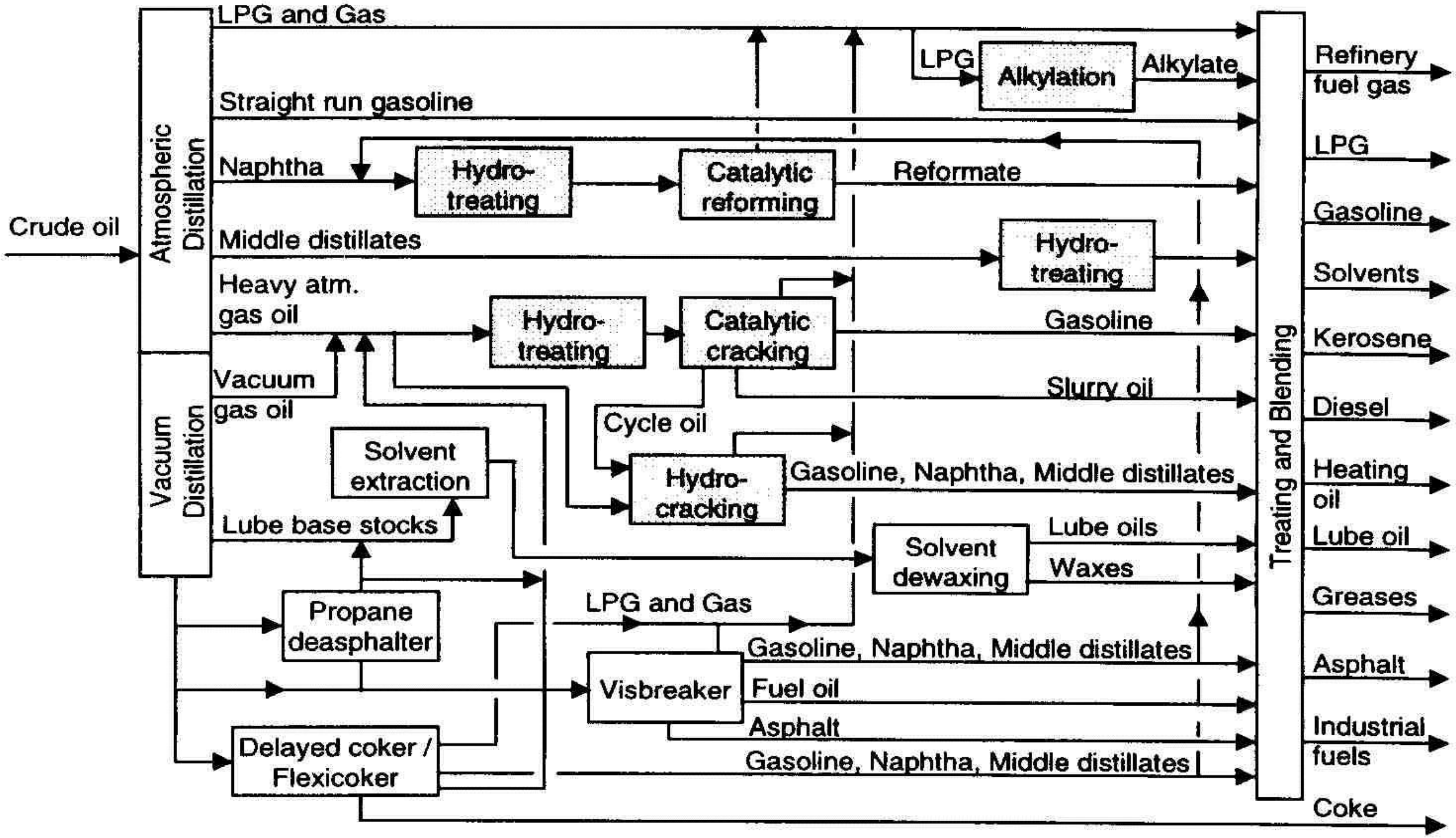
Refining operations

4. **Formulating and Blending** is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties.
5. **Other Refining Operations** include:
   - light-ends recovery;
   - sour-water stripping;
   - solid waste, process-water and wastewater treatment;
   - cooling, storage and handling and product movement;
   - hydrogen production;
   - acid and tail-gas treatment;
   - and sulfur recovery.

Refining operations

- **Auxiliary Operations and Facilities** include:
  - light steam and power generation;
  - process and fire water systems;
  - flares and relief systems;
  - furnaces and heaters;
  - pumps and valves;
  - supply of steam, air, nitrogen, and other plant gases;
  - alarms and sensors;
  - noise and pollution controls;
  - sampling, testing, and inspecting and laboratory;
  - control room;
  - maintenance; and
  - administrative facilities.

Flow scheme of a modern refinery



Physical and chemical processes

Physical	Chemical	
	Thermal	Catalytic
Desalting/dehydrating Distillation Solvent extraction Propane deasphalting Solvent dewaxing Blending	Visbreaking Delayed coking Flexicoking	Hydrotreating Catalytic reforming Catalytic cracking Hydrocracking Catalytic dewaxing Alkylation Polymerization Isomerization

Physical Processes

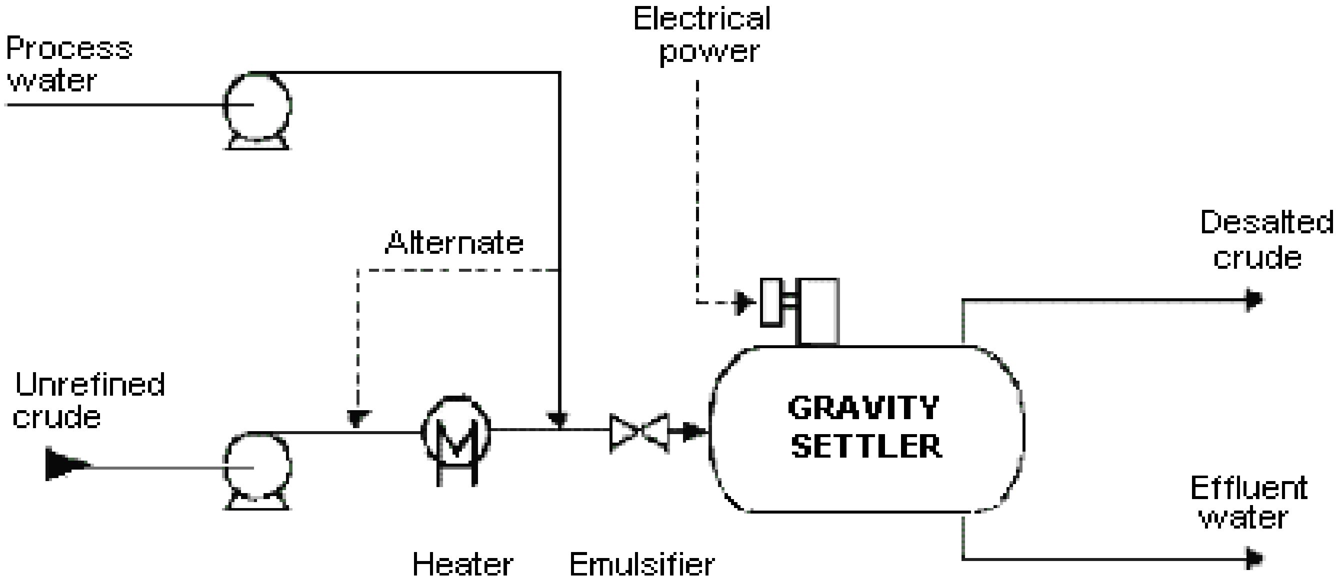
- Desalting/dehydration
- Crude distillation
- Propane deasphalting
- Solvent extraction
- Solvent dewaxing
- Blending

Desalting/Dehydration$^{1/2}$

- Process Objective:
  - Remove the contaminants in crude oil (often contains water, inorganic salts, suspended solids, and water-soluble trace metals) so as to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning catalysts in processing units.
- Primary Process Technique:
  - The **two** most typical methods of crude-oil desalting are chemical and electrostatic separation, and both use hot water as the extraction agent.
- Process steps:
  - The crude oil feedstock is heated to 65-180°C to reduce viscosity and surface tension for easier mixing and separation of the water
  - In chemical desalting, water and chemical surfactant (demulsifiers) are added to the crude, which is heated so that salts and other impurities dissolve or attach to the water, then held in a tank to settle out.
  - Electrical desalting is the application of high-voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids.

Desalting/Dehydration$^{2/2}$

- The crude oil feedstock is heated to 65-180°C to reduce viscosity and surface tension for easier mixing and separation of the water. The temperature is limited by the vapor pressure of the crude-oil feedstock.
- In both methods other chemicals may be added. Ammonia is often used to reduce corrosion. Caustic or acid may be added to adjust the pH of the water wash.



Crude Distillation

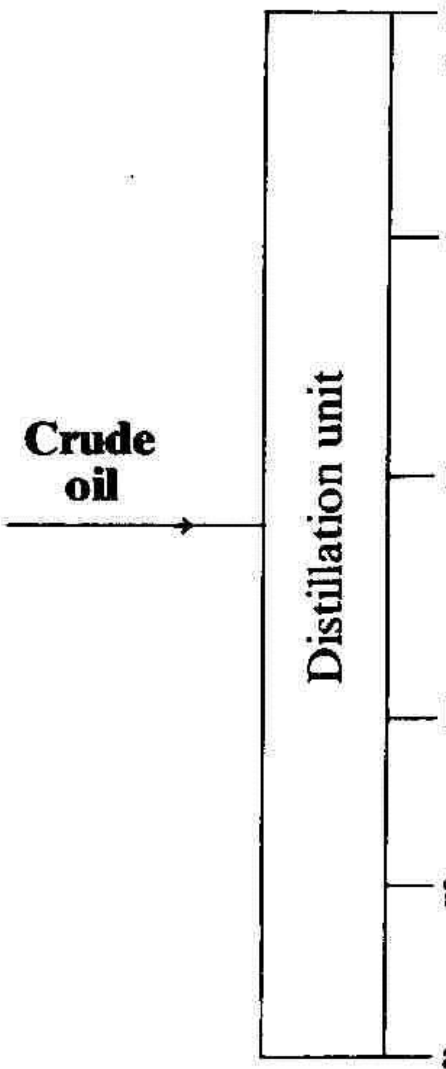
- Step 1 in the refining process is the separation of crude oil into various fractions or straight-run cuts by distillation in

  1- atmospheric and

  2- vacuum towers.

  The main fractions or "cuts" obtained have specific boiling-point ranges and can be classified in order of decreasing volatility into gases, light distillates, middle distillates, gas oils, and residuum.

Fraction of Petroleum



Fraction	b.p.	*Fuel applications*
gases CH_4, C_2H_6, C_3H_8, C_4H_{10}	b.p. <20°C	Refinery fuel. Liquefied petroleum gas (propane and butane).
straight-run gasoline	b.p. 30–75 °C	Has comparatively low octane number. Used for blending in motor gasoline.
naphtha	b.p. 75–190 °C	Octane number too low for use in motor gasoline. Little direct use as fuel.
kerosine	b.p. 190–250 °C	Domestic fuel ('paraffin'), jet fuel, tractor fuel.
gas oil	b.p. 250–350 °C	Diesel fuel, central heating fuel.
atmospheric residue	b.p. > 350 °C	Fuel for power stations, ships, and large heating installations.

Table 7.3 Fractions of Petroleum

Approximate bp (°C)	Name	Uses
<20°C	Gases	CH_4, C_2H_6, C_3H_8, C_4H_{10}—similar to natural gas and useful for fuel and chemicals.
20-150°C	Light naphtha (mainly C_5-C_6)	C_4-C_{10} aliphatic and cycloaliphatic compounds. May contain some aromatics. Useful for both fuel and chemicals.
150-200°C	Heavy naphtha (mainly C_7-C_9)	C_4-C_{10} aliphatic and cycloaliphatic compounds. May contain some aromatics. Useful for both fuel and chemicals.
175-275°C	Kerosene	Contains C_9-C_{16} compounds useful for jet, tractor, and heating fuel.
200-400°C	Gas oil	Contains C_{15}-C_{25} compounds useful for diesel and heating fuel. Catalytically cracked to naphtha and steam-cracked to olefins.
>350°C	Lubricating oil	Used for lubrication. May be catalytically cracked to lighter fractions.
>350°C	Heavy fuel oil	Boiler fuel. May be catalytically cracked to lighter fractions.
	Asphalt	Paving, coating, and structural uses.

Hydrocarbon	Octane number[a]		Boiling point (K)
	RON	MON	
n-Pentane	62		309
2-Methylbutane	90		301
Cyclopentane	85		322
n-Hexane	26		342
2-Methylpentane	73		333
2,2-Dimethylbutane	93		323
1-Hexene	63		337
2-Hexene	81		341
Benzene	>100		353
Cyclohexane	77		354
***n*-Heptane**	**0**[b]		**362**
2-methylheptane	13		381
2,2,4-Trimethylpentane	**100**[b]		**372**
1-Octene	35		395
2-Octene	56		398
3-Octene	68		396
Xylenes	>100		≈415
Ethylbenzene	98		410
1,2-Dimethylcyclohexane	79		403
Ethylcyclohexane	41		403
Methyl-tertiary-butyl-ether (MTBE)	118		328
Ethyl-tertiary-butyl-ether (ETBE)	118		345
Tertiary-amyl-methyl-ether (TAME)	111		359
Light straight-run gasoline	68	67	
Isomerate	85	82	
FCC light gasoline	93	82	
FCC heavy gasoline	95	85	
Alkylate	95	92	
Reformate (CCR)	99	88	

[a] Research octane number (RON). The motor octane number (MON) is generally lower, depending on the particular compound. The difference is particularly large for alkenes and aromatics.

[b] By definition.

Crude Distillation Unit: Atmospheric distillation 1/2

- Process Objective:
  - To distill and separate valuable distillates (naphtha, kerosene,diesel) and atmospheric gas oil (AGO) from the crude feedstock.
- Primary Process Technique:
  - Complex distillation
- Process steps:
  - Preheat the desalted crude feed by utilizing recovered heat from the product streams
  - The feedstock then flows to a direct-fired crude charge heater then into the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 340-370°C (above these temperatures undesirable thermal cracking may occur).

Crude Distillation Unit: Atmospheric distillation^{2/2}

- As the hot vapor rises in the tower, its temperature is reduced.

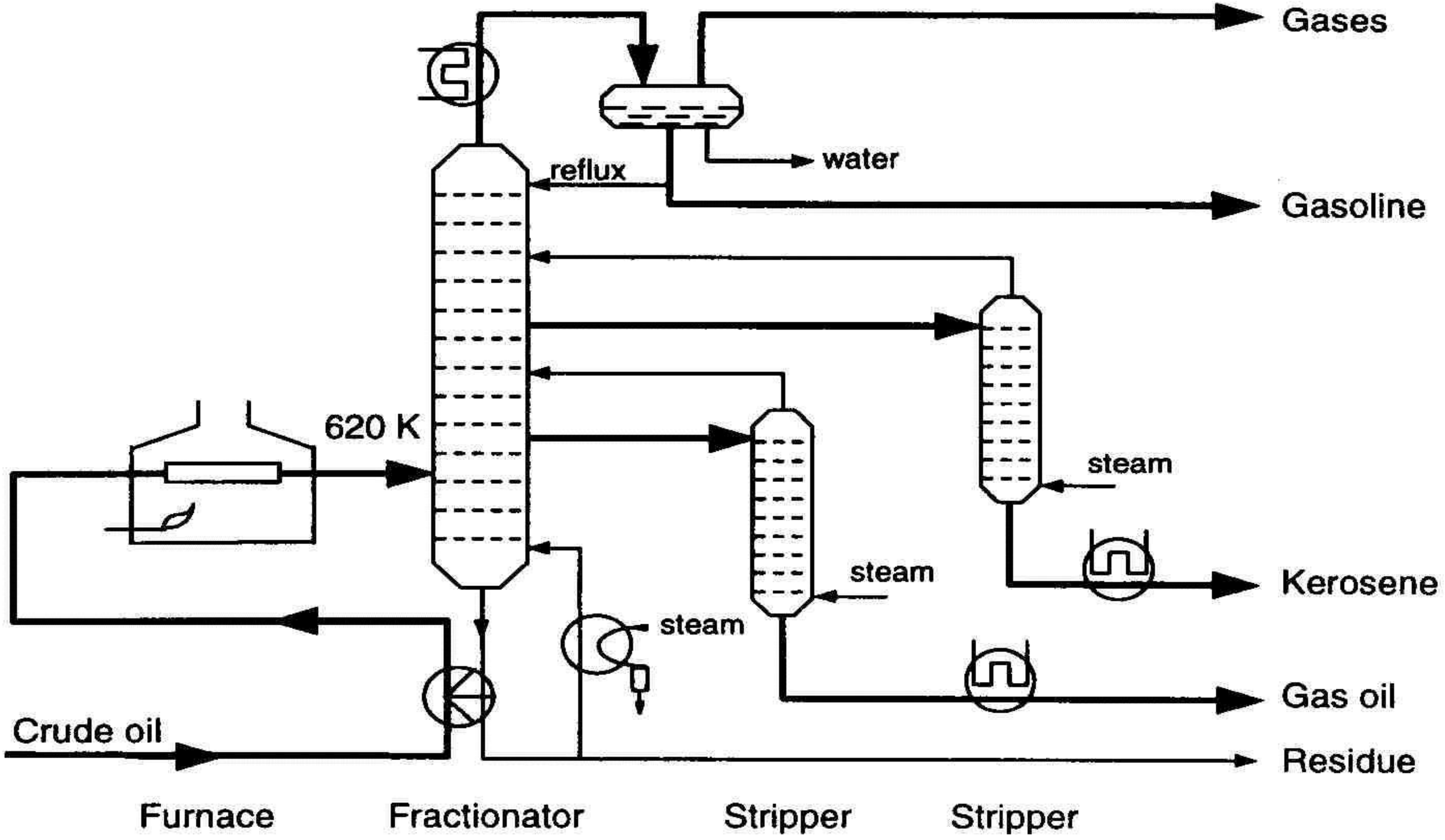
- Heavy fuel oil or asphalt residue is taken from the bottom.

- At successively higher points on the tower, the various major products including lubricating oil, heating oil, kerosene, gasoline, and uncondensed gases (which condense at lower temperatures) are drawn off.

- Product draws are on the top, sides, and bottom

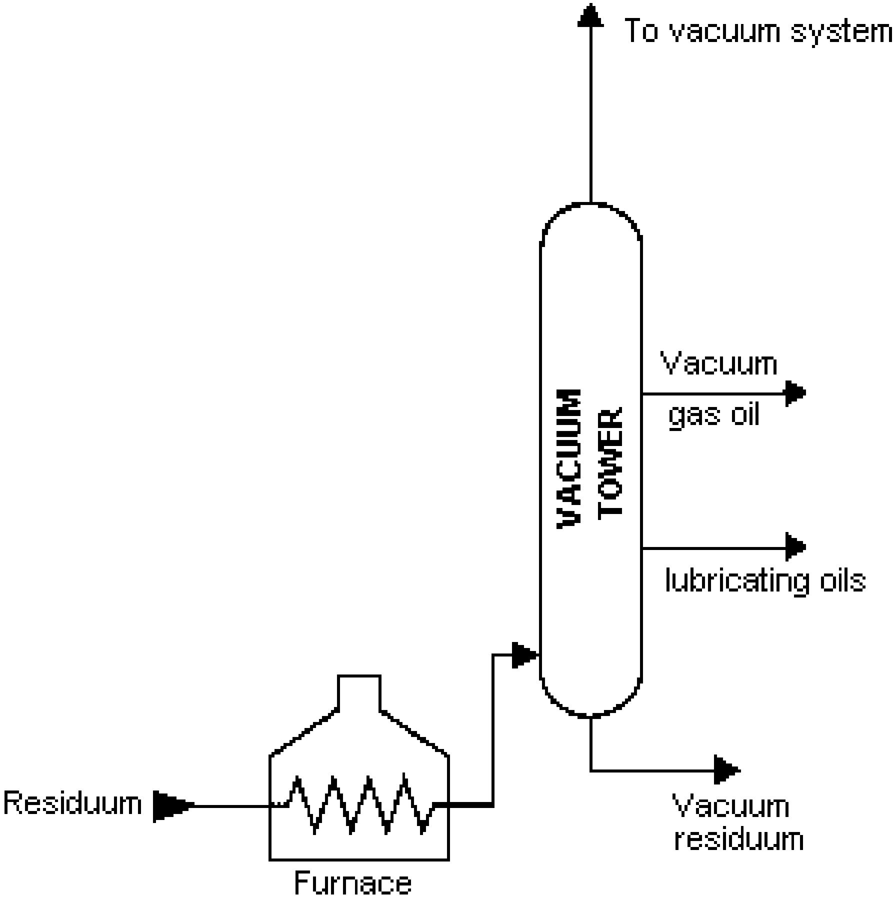
- Utilize pump around cooling loops to create internal liquid reflux

Simple Crude Distillation Unit

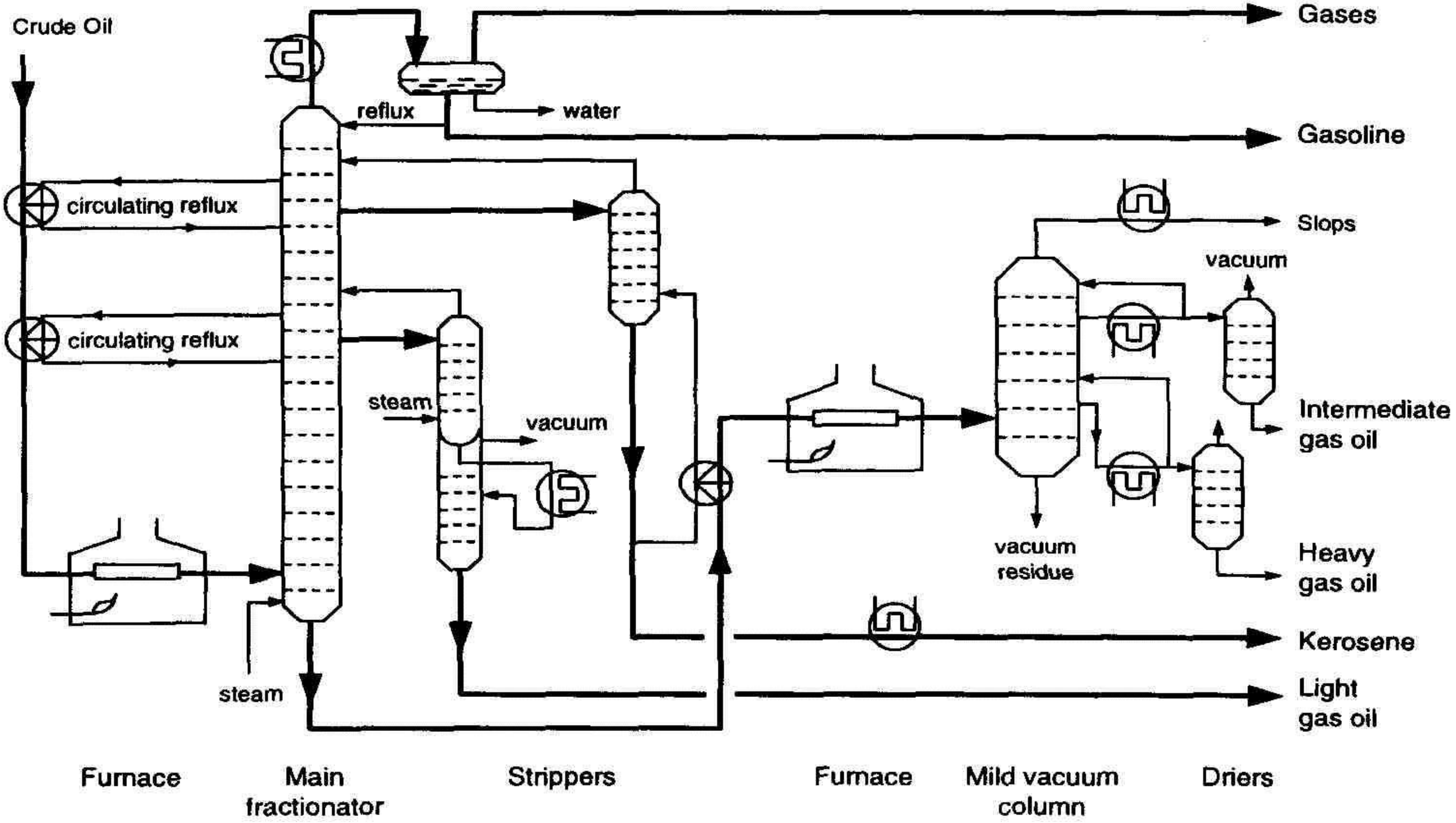


Crude Distillation Unit: Vacuum Distillation$^{2/2}$

- **Process Objective:**
  - To further distill the residuum from the atmospheric tower without thermal cracking,
  - A typical first-phase vacuum tower may produce gas oils, lubricating-oil base stocks, and heavy residual for propane deasphalting
- **Primary Process Technique:**
  - Reduced pressure is required.
  - The process takes place in one or more vacuum distillation towers
- **Process steps:**
  - Preheat residuum feed in a fired furnace
  - Introduce the feed to a tower at reduced pressure evacuated by a vacuum pumps or ejectors



Modern crude distillation



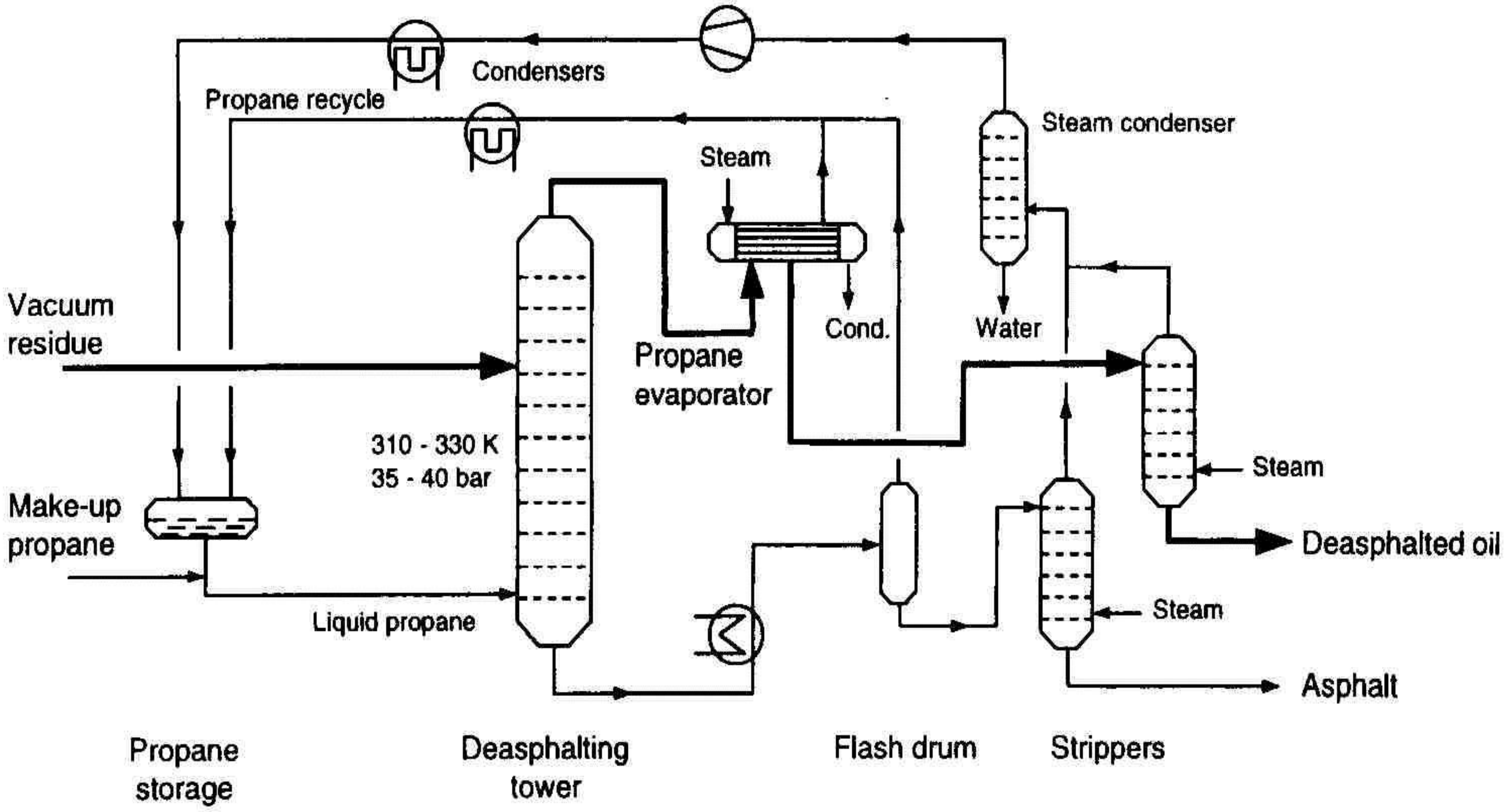
Propane Deasphalting

- **Process Objective**: Coke-forming tendencies of heavier distillation products are reduced by removal of asphaltenic materials by solvent extraction.
- **Primary Process Technique**: Liquid propane is a good solvent (butane and pentane are also commonly used). Deasphalting is based on solubility of hydrocarbons in propane
- **Process steps**: Vacuum residue is fed to a countercurrent deasphalting tower.

  Alkanes dissolve in propane whereas asphaltenic materials (aromatic compounds), 'coke-precursors' do not.

  Asphalt is sent for thermal processing.

Propane Deasphalting



Solvent Extraction and Dewaxing

- Solvent treating is a widely used method of refining

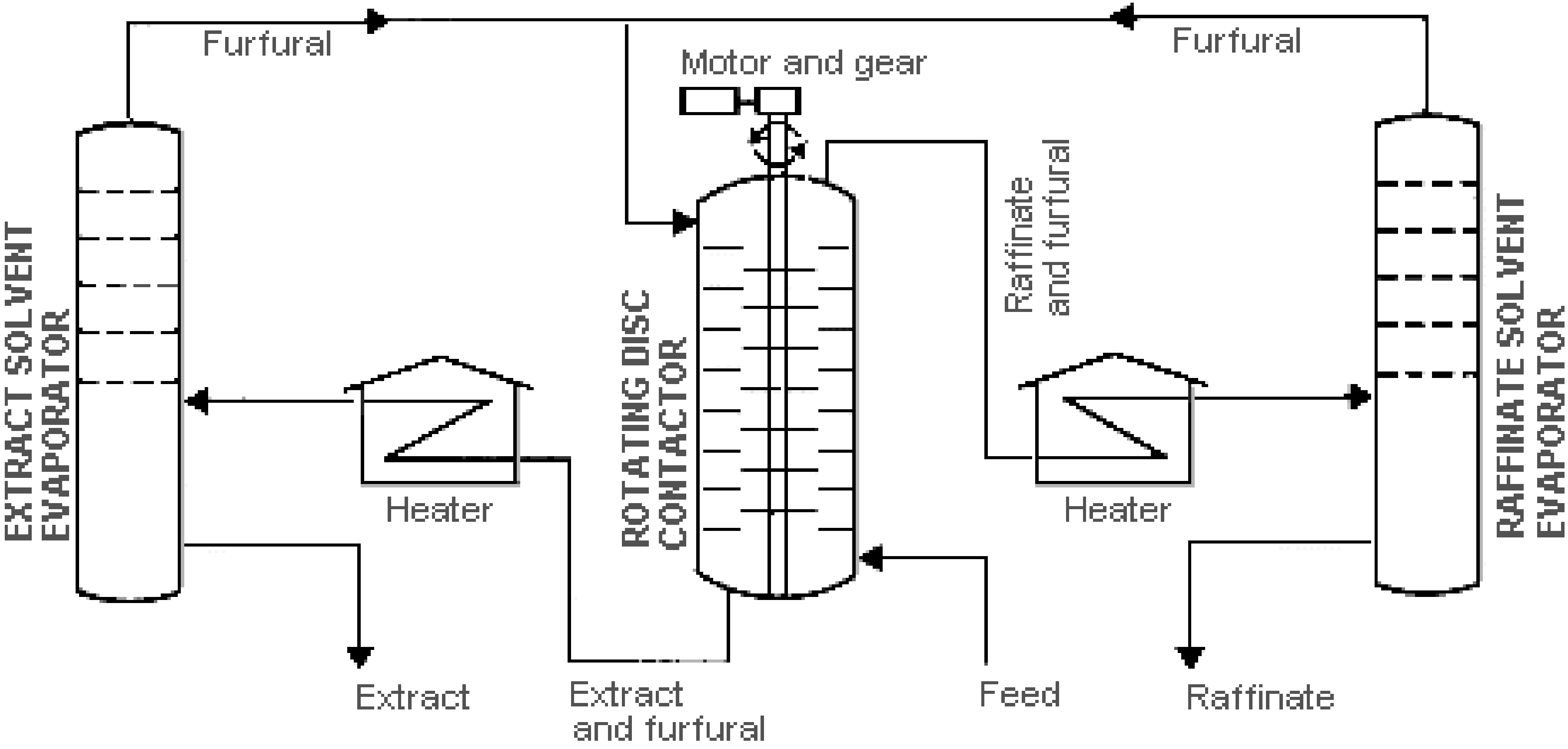
  1- lubricating oils 2- a host of other refinery stocks.

- Since distillation (fractionation) separates petroleum products into groups only by their boiling-point ranges, impurities may remain. These include organic compounds containing sulfur, nitrogen, and oxygen; inorganic salts and dissolved metals; and soluble salts that were present in the crude feedstock.
- In addition, kerosene and distillates may have trace amounts of aromatics and naphthenes, and lubricating oil base-stocks may contain wax.
- Solvent refining processes including solvent extraction and solvent dewaxing usually remove these undesirables at intermediate refining stages or just before sending the product to storage.

Solvent Extraction 1/3

- Process Objective:
  - to prevent corrosion, protect catalyst in subsequent processes, and improve finished products by removing unsaturated, aromatic hydrocarbons from lubricant and grease stocks.
- Primary Process Technique:
  - The solvent extraction process separates aromatics, naphthenes, and impurities from the product stream by dissolving or precipitation.
  - The most widely used extraction solvents are phenol and furfural.
- Process steps:
  - In one type of process, the feedstock is washed with furfural in which the substances to be removed are more soluble than in the desired resultant product.
  - The solvent is separated from the product stream by heating, evaporation, or fractionation, and residual trace amounts are subsequently removed from the raffinate by steam stripping or vacuum flashing.
  - The solvent is regenerated for reused in the process.

Solvent Extraction 2/3



Aromatic Solvent Extraction Unit

Solvent Extraction 3/3

- In another process, selected solvents are added to cause impurities to precipitate out of the product.
- In the adsorption process, highly porous solid materials collect liquid molecules on their surfaces

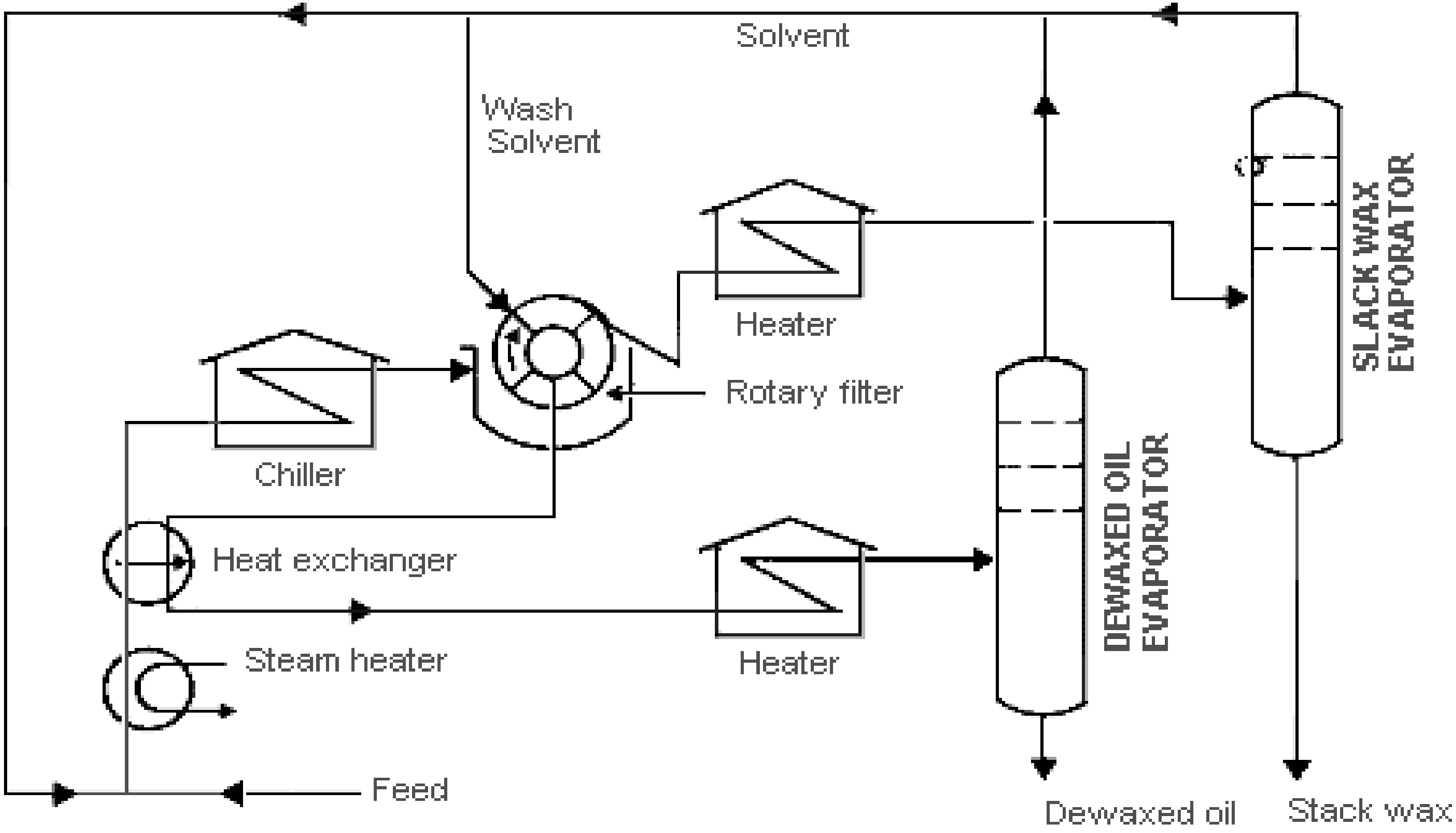
- Electric precipitation may be used for separation of inorganic compounds.
- The most widely used extraction solvents are phenol, furfural, and cresylic acid.
- Other solvents less frequently used are liquid sulfur dioxide, nitrobenzene, and 2,2' dichloroethyl ether.
- The selection of specific processes and chemical agents depends on the nature of the feedstock being treated, the contaminants present, and the finished product requirements.

Solvent Dewaxing

- Process Objective:
  - Solvent dewaxing is used to remove wax from either distillate or residual base stock at any stage in the refining process.
- Primary Process Technique:
  - Usually two solvents are used: toluene, which dissolves the oil and maintains fluidity at low temperatures, and methyl ethyl ketone (MEK), which dissolves little wax at low temperatures and acts as a wax precipitating agent. Other solvents sometimes used include benzene, methyl isobutyl ketone, propane, petroleum naphtha, ethylene dichloride, methylene chloride, and liquid sulfur dioxide.
- Process steps:

  There are several processes in use for solvent dewaxing, but all have the same general steps, which are:
  - Mixing the feedstock with a solvent;
  - Precipitating the wax from the mixture by chilling;
  - Recovering the solvent from the wax and dewaxed oil for recycling by distillation and steam stripping.

Solvent Dewaxing Unit



Blending

- Process Objective:
  - Blending is the physical mixture of a number of different liquid hydrocarbons to produce a finished product with certain desired characteristics.
- Primary Process Technique:
  - Products can be blended in-line through a manifold system, or batch blended in tanks and vessels.
  - Additives including octane enhancers, anti-oxidants, anti-knock agents, gum and rust inhibitors, detergents, *etc.* are added during and/or after blending to provide specific properties not inherent in hydrocarbons.
- Process steps:
  - In-line blending of gasoline, distillates, jet fuel, and kerosene is accomplished by injecting proportionate amounts of each component into the main stream where turbulence promotes thorough mixing.

THERMAL PROCESSES

- When a hydrocarbon is heated to a sufficiently high temperature ***thermal cracking*** occurs. This is sometimes referred to as *pyrolysis* (especially when coal is the feedstock).
- When steam is used for heating it is called ***steam cracking***.
- There are two thermal processes used in refineries.
- **Visbreaking**
- **Delayed coking**

Visbreaking 1/2

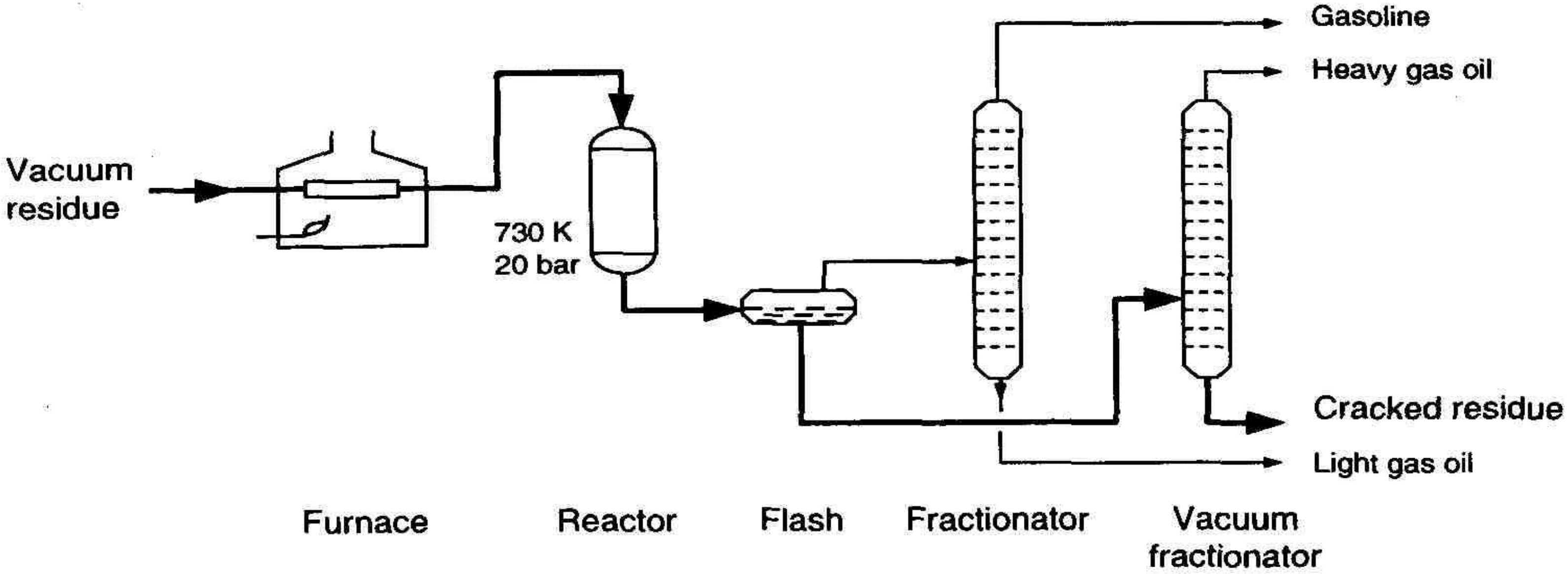
Visbreaking is a mild form of thermal cracking to lower the viscosity

- **Process Objective**:
  - Lowers the viscosity of heavy crude-oil residues without affecting the boiling point range.
  - Reduce the pour point of waxy residues and reduce the viscosity of residues used for blending with lighter fuel oils.
- **Primary Process Technique**:

  Visbreaking is a mild form of thermal cracking for which oil is heated to a sufficiently high temperature
- **Process steps**:
  - Residuum from the atmospheric distillation tower is heated (425-510ºC) at atmospheric pressure and mildly cracked in a heater.
  - It is then quenched with cool gas oil to control over-cracking, and flashed in a distillation tower.

Visbreaking 2/2

- Alternatively, vacuum residue can be cracked. The severity of the visbreaking depends upon temperature and reaction time (1-8 min).
- Usually < 10 wt% of gasoline and lighter products are produced.



Delayed Coking Process $^{1/3}$

- Coking is a severe method of thermal cracking used to upgrade heavy residuals into lighter products or distillates.
- Coking produces straight-run gasoline (*Coker naphtha*) and various middle-distillate fractions used as catalytic cracking feedstock.
- The process completely reduces hydrogen so that the residue is a form of carbon called *"coke."*
- Three typical types of coke are obtained (*sponge coke, honeycomb coke, and needle coke*) depending upon the reaction mechanism, time, temperature, and the crude feedstock.
- In delayed coking the heated charge (typically residuum from atmospheric distillation towers) is transferred to large coke drums which provide the long residence time needed to allow the cracking reactions to proceed to completion.

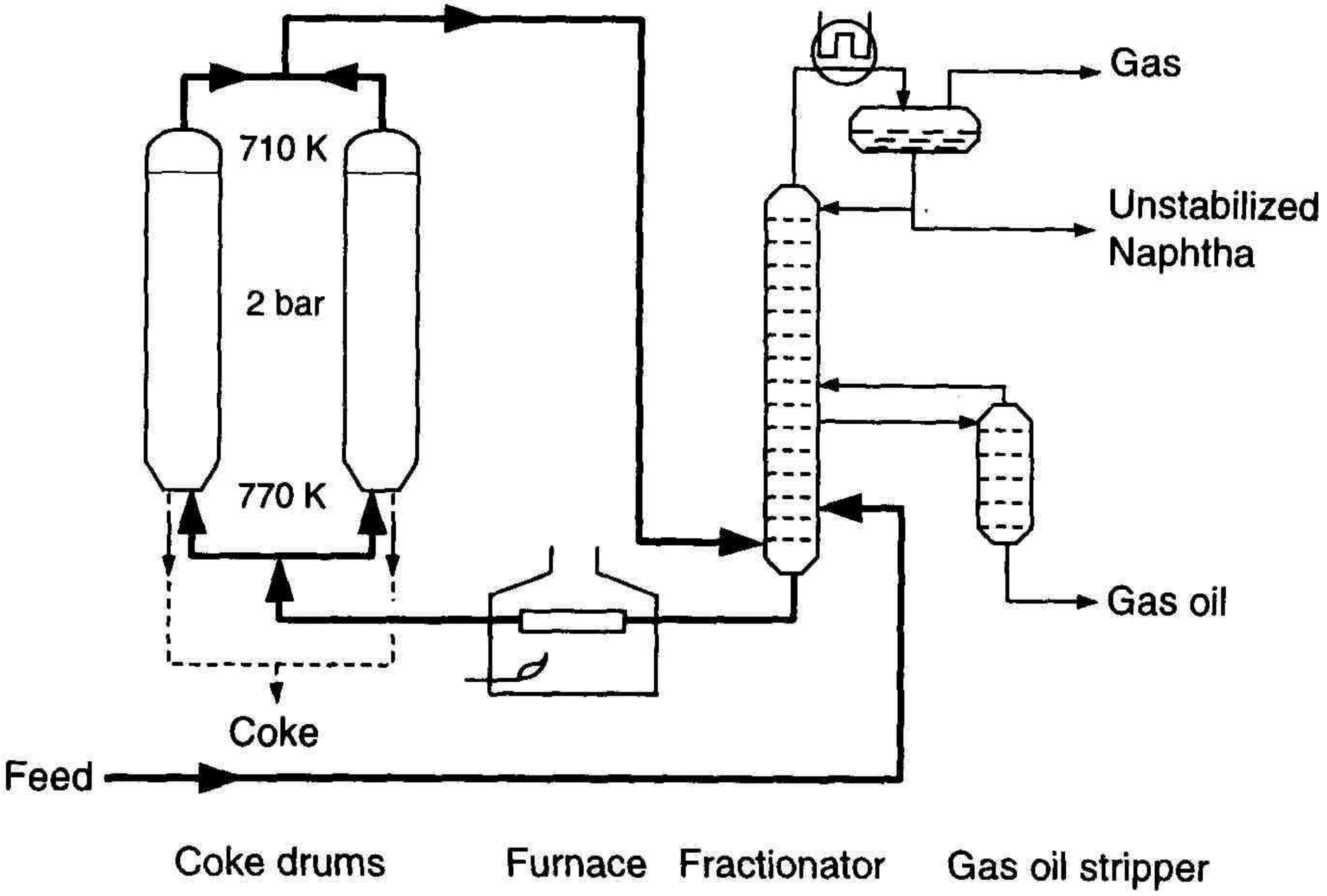
Delayed Coking Process $^{2/3}$

- Process Objective:
  - To convert low value residue to valuable products such as naphtha and diesel and gas oil (ie used to upgrade heavy residuals into lighter products or distillates).
- Primary Process Technique:
  - The process completely reduces hydrogen so that the residue is a form of carbon called *"coke."* in a semi batch process.

Delayed Coking Process $^{3/3}$

- Process steps:
  - In delayed coking, the heated residuum from atmospheric towers is transferred into large coke drums which provide the long residence time needed to allow the cracking reactions to proceed to completion.
  - The bottoms of the fractionator are fed to coker drums via a furnace where the hot material (440°-500°C) is held approximately 24 hours (delayed) at pressures of 2-5 bar, until it cracks into lighter products.
  - Vapors from the drums are returned to a fractionator where gas, naphtha, and gas oils are separated out. The heavier hydrocarbons produced in the fractionator are recycled through the furnace.
  - After the coke reaches a predetermined level in one drum, the flow is diverted to another drum in order to maintain continuous operation.
  - To strip out uncracked hydrocarbons, the full drum is steamed, cooled by water injection, and de-coked by mechanical or hydraulic methods.
  - The coke is mechanically removed by an auger rising from the bottom of the drum. Hydraulic decoking consists of fracturing the coke bed with high-pressure water ejected from a rotating cutter.

Delayed Coking/ Process Schematic



CATALYTIC PROCESSES

There are several types of catalytic processes used in refineries.

- Fluid Catalytic Cracking (FCC)
- Hydrotreating
- Hydrocracking
- Catalytic Reforming
- Alkylation

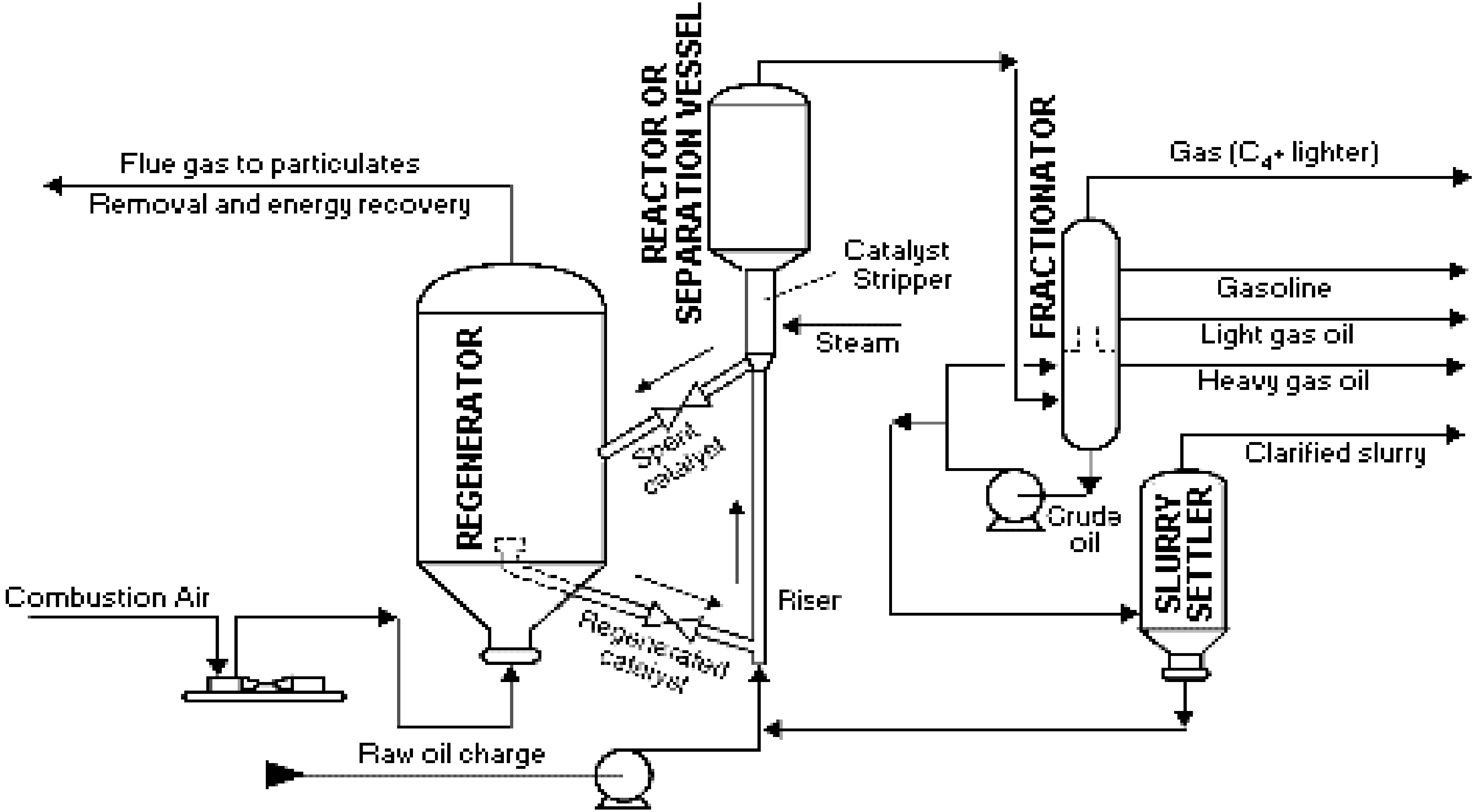
Fluid Catalytic Cracking$^{1/3}$

- Process Objective:
  - To convert low value gasoil to valuable products (gasoline, naphtha and diesel)
- Primary Process Technique:
  - Catalytic cracking increases H/C ratio by carbon rejection
  - Thermal cracking occurs on the surface of the catalyst in a continuous process.
- Process steps:
  - Gas oil feed and catalyst are dispersed into the bottom of the riser using steam
  - Oil is cracked in the presence of a finely divided catalyst, which is maintained in an aerated or fluidized state by the oil vapours.
  - Preheated feed is mixed with hot, regenerated catalyst in the riser and combined with a recycle stream, vapourized, and raised to reactor temperature (485-540°C) by the hot catalyst
  - As the mixture travels up the riser, the charge is cracked at 0.7-2 bar.
  - The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapors, and steam as the conveying media.

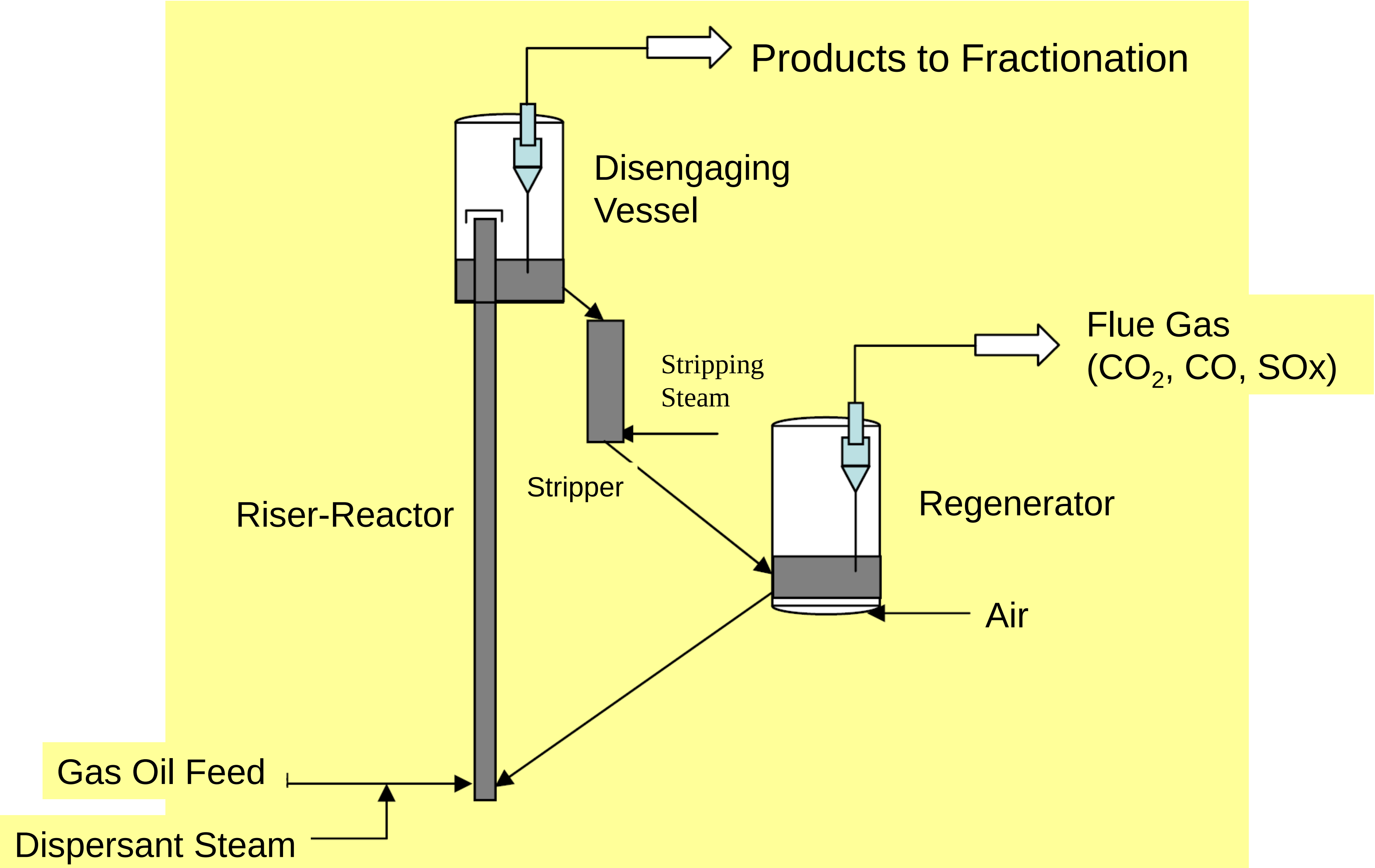
Fluid Catalytic Cracking$^{2/3}$

- Disengaging drum separates spent catalyst from product vapors
- Steam strips residue hydrocarbons from spent catalyst
- Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits will burn off at the bottom where preheated air and spent catalyst are mixed.
- Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process.
- Regenerated catalyst enters bottom of riser-reactor

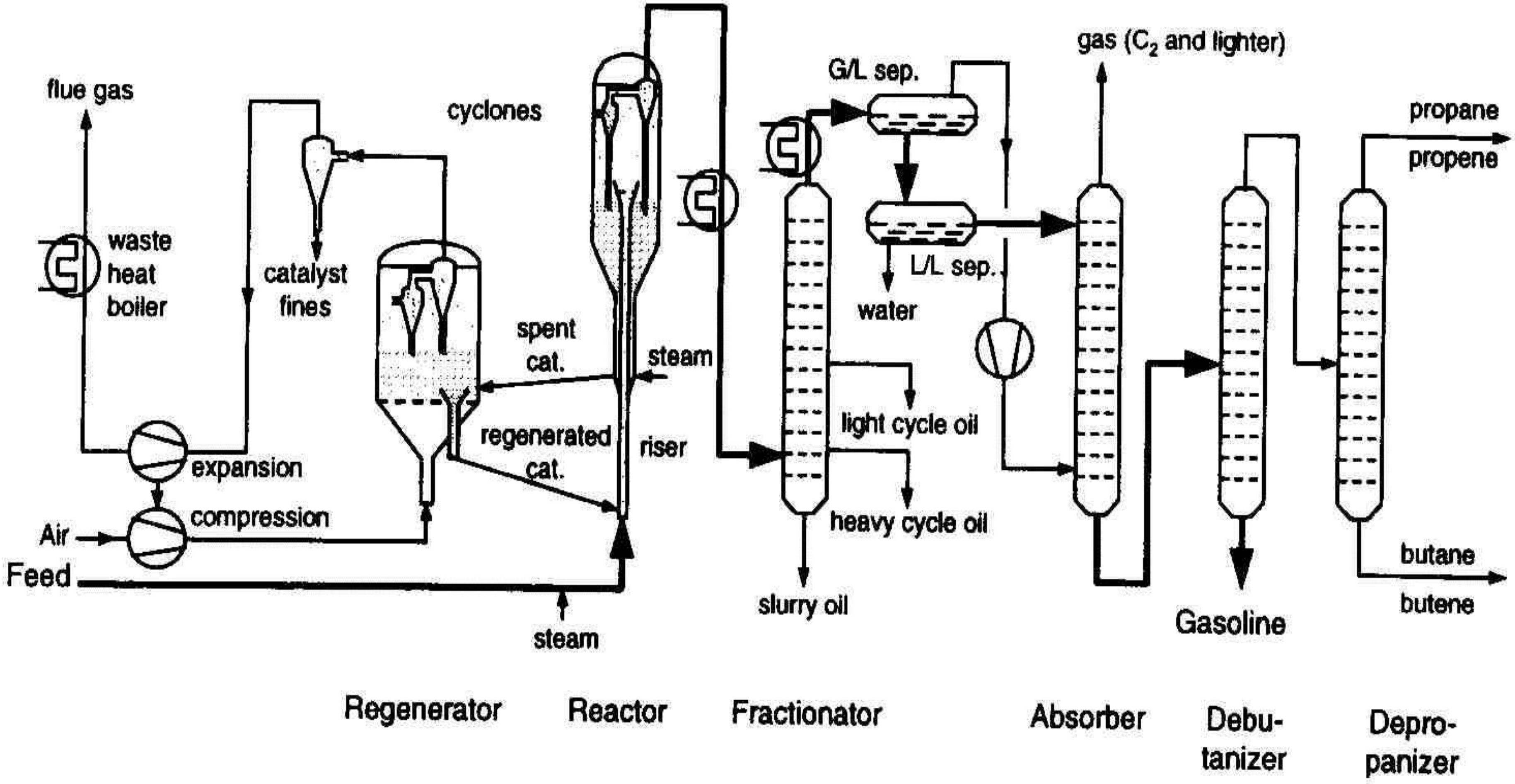
Fluid Catalytic Cracking$^{3/3}$



Fluidic Catalytic Cracking-Process Schematic



Fluid Catalytic Cracking- Full Process

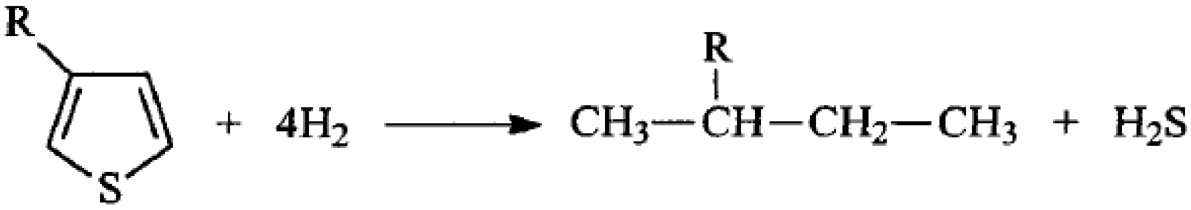


Hydrotreating Processes$^{1/2}$

- Catalytic hydrotreating is a hydrogenation process used to remove about 90% of contaminants such as nitrogen, sulfur, oxygen, and metals from liquid petroleum fractions. Such as Remove NH_3

$$R-CH_2-CH_2-CH_2-NH_2 + H_2 \longrightarrow R-CH_2-CH_2-CH_3 + NH_3$$

- Also, catalytic hydrotreating converts olefins and aromatics to saturated compounds, such as:

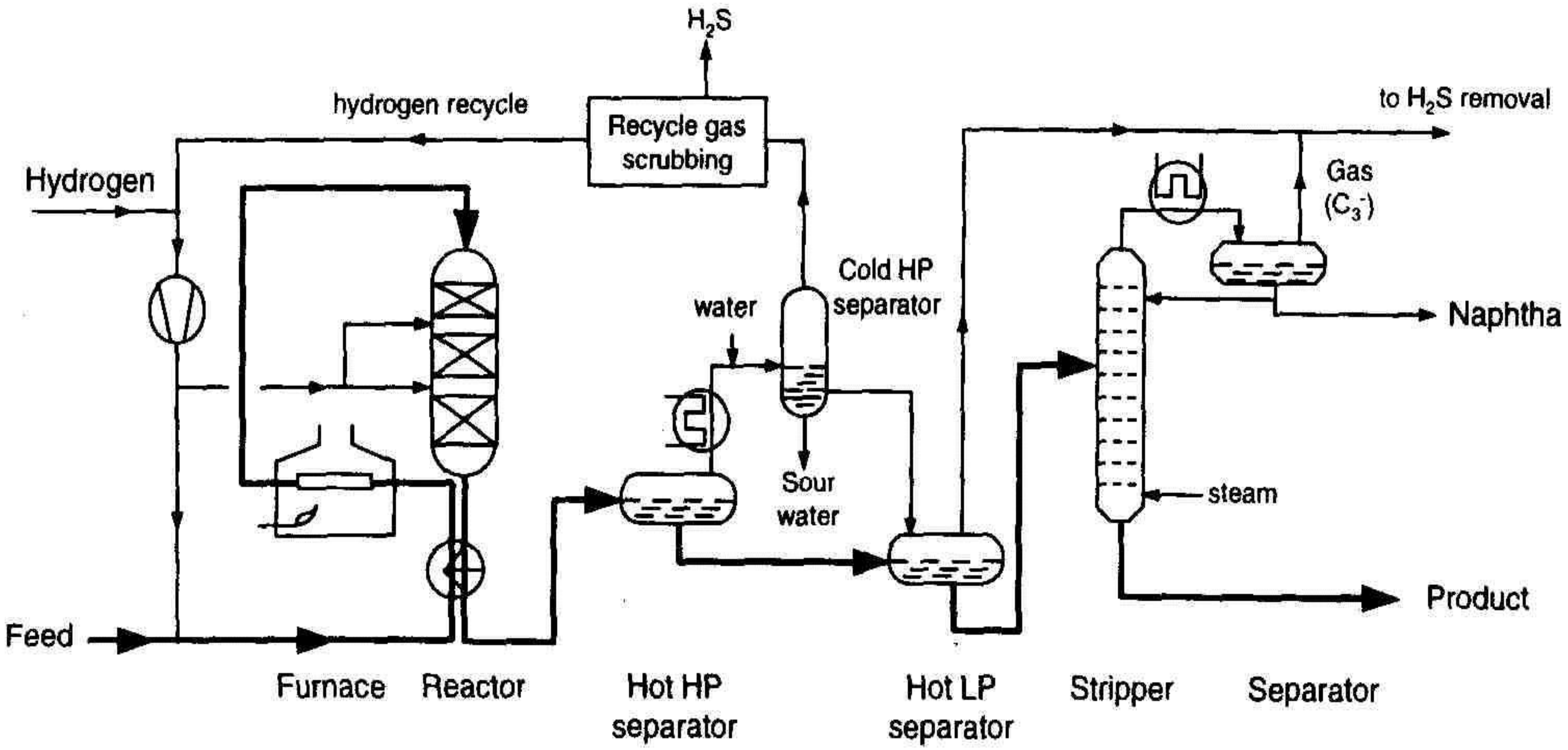


- Typically, hydrotreating is done prior to processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock.

Hydrotreating Processes$^{2/2}$

- Process Objective:
  - To remove contaminants (sulfur, nitrogen, metals) and saturate olefins and aromatics to produce a clean product for further processing or finished product sales.
- Primary Process Technique:
  - Hydrogenation occurs in a fixed catalyst bed to improve H/C ratios and to remove sulfur, nitrogen, and metals.
- Process steps:
  - Feed is preheated using the reactor effluent
  - Hydrogen is combined with the feed and heated to the desired hydro-treating temperature using a fired heater (at 285-34O^{0}C)
  - Feed and hydrogen pass downward in a hydrogenation reactor packed with various types of catalyst depending upon reactions desired (such as cobalt or nickel oxide/molybdenum oxide catalyst)
  - Reactor effluent is cooled and enter the high pressure separator which separates the liquid hydrocarbon from the hydrogen/hydrogen sulfide/ammonia gas
  - Acid gases are absorbed from the hydrogen in the amine absorber
  - Hydrogen is recycled with make-up hydrogen
  - Further separation of LPG gases occurs in the low pressure separator prior to sending the hydrocarbon liquids to fractionation

Hydrotreating: flow scheme



Hydrotreating Processes

- Naphtha Hydrotreating
  - Primary objective is to remove sulfur contaminant for downstream processes; typically < 1wppm
- Gasoline Hydrotreating
  - Sulfur removal from gasoline blending components to meet recent clean fuels specifications
- Mid-Distillate Hydrotreating
  - Sulfur removal from kerosene for home heating
  - Convert kerosene to jet via mild aromatic saturation
  - Remove sulfur from diesel for clean fuels
- FCC Feed Pretreating
  - Nitrogen removal for better FCC catalyst activity
  - Sulfur removal for Sulfur oxide reduction in the flue gas and easier post-FCC treatment
  - Aromatic saturation improves FCC feed “crackability”
  - Improved H/C ratios increase FCC capacity and conversion

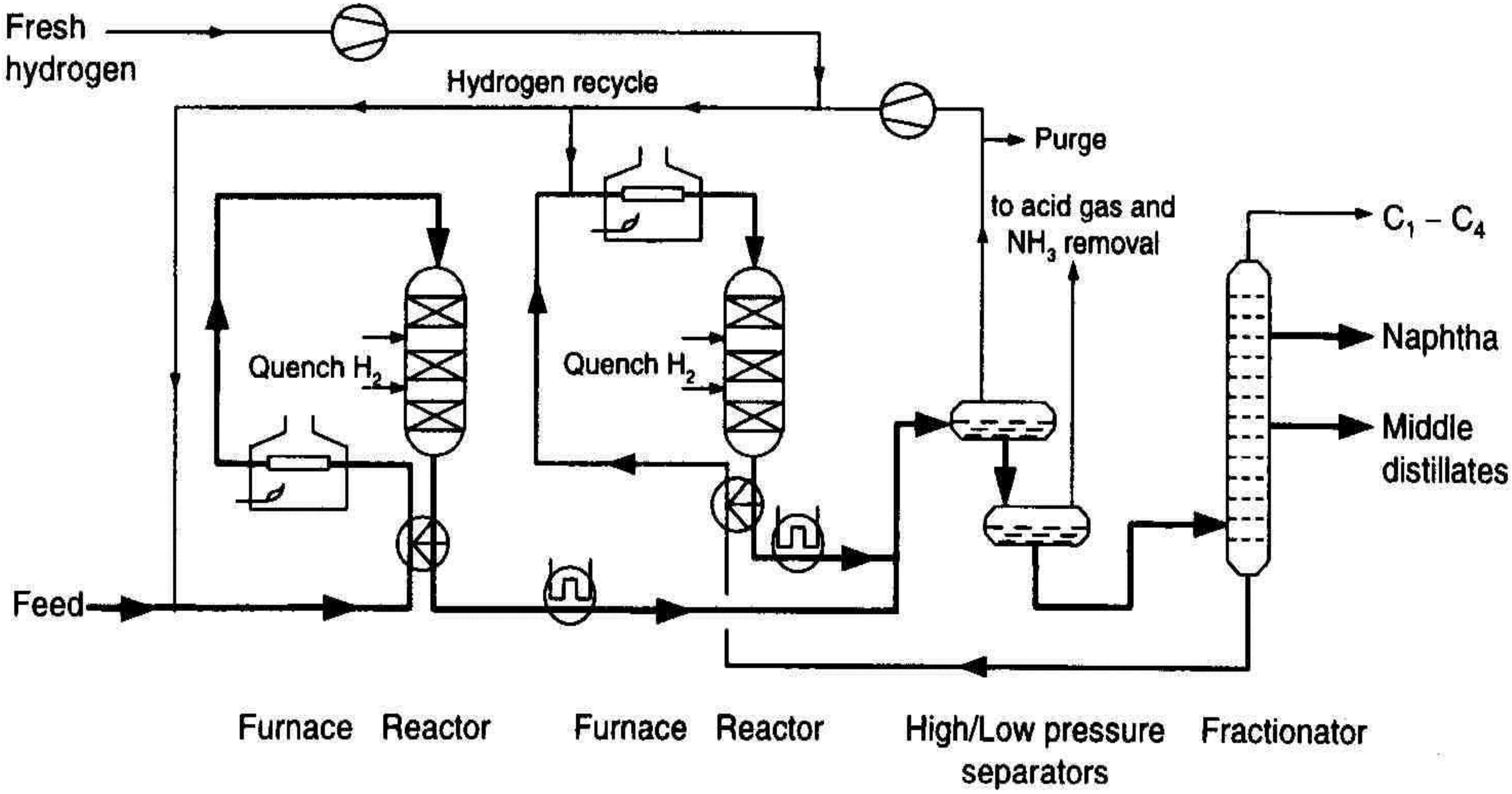
Hydrocracking

- Hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feedstock is cracked in the presence of hydrogen to produce more desirable products.
- The process employs (1) high pressure, (2) high temperature, (3) a catalyst, and (4) hydrogen.
- Hydrocracking is used for feedstock that are difficult to process by either catalytic cracking or reforming, since these feedstock are characterized usually by
  - i) a high polycyclic aromatic content
  - ii) high concentrations of the two catalyst poisons: sulfur and nitrogen
- The process largely depends on the nature of the feedstock and the relative rates of the two competing reactions: hydrogenation and cracking.
- Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (70-140 bar) and fairly high temperatures (400°-800°C), in the presence of hydrogen and special catalysts.

Hydrocracking Process

- Process Objective:
  - To remove feed contaminants (nitrogen & sulfur) and to convert low value gas oils to valuable products (naphtha, middle distillates, and ultra-clean lube base stocks).
- Primary Process Technique:
  - Hydrogenation occurs in fixed hydrotreating catalyst beds to improve H/C ratios and to remove sulfur, nitrogen, and metals. This is followed by one or more reactors with fixed hydrocracking catalyst beds to dealkylate aromatic rings, open naphthene rings, and hydrocrack paraffin chains.
- Process steps:
  - Preheated feed is mixed with hot hydrogen and passes through a multi-bed reactor with inter-stage hydrogen quenches for hydrotreating
  - The catalysts convert sulfur and nitrogen compounds to H_2S and NH_3. Limited hydrocracking also occurs.
  - Reactor effluents are combined and pass through high and low pressure separators and are fed to the fractionator where valuable products are drawn from the top, sides, and bottom
  - Fractionator bottoms may be recycled to a second pass hydrocracker for additional conversion all the way up to full conversion the operations of the second stage are more severe (higher temperatures and pressures). Again, the second stage product is separated from the hydrogen and charged to the fractionator

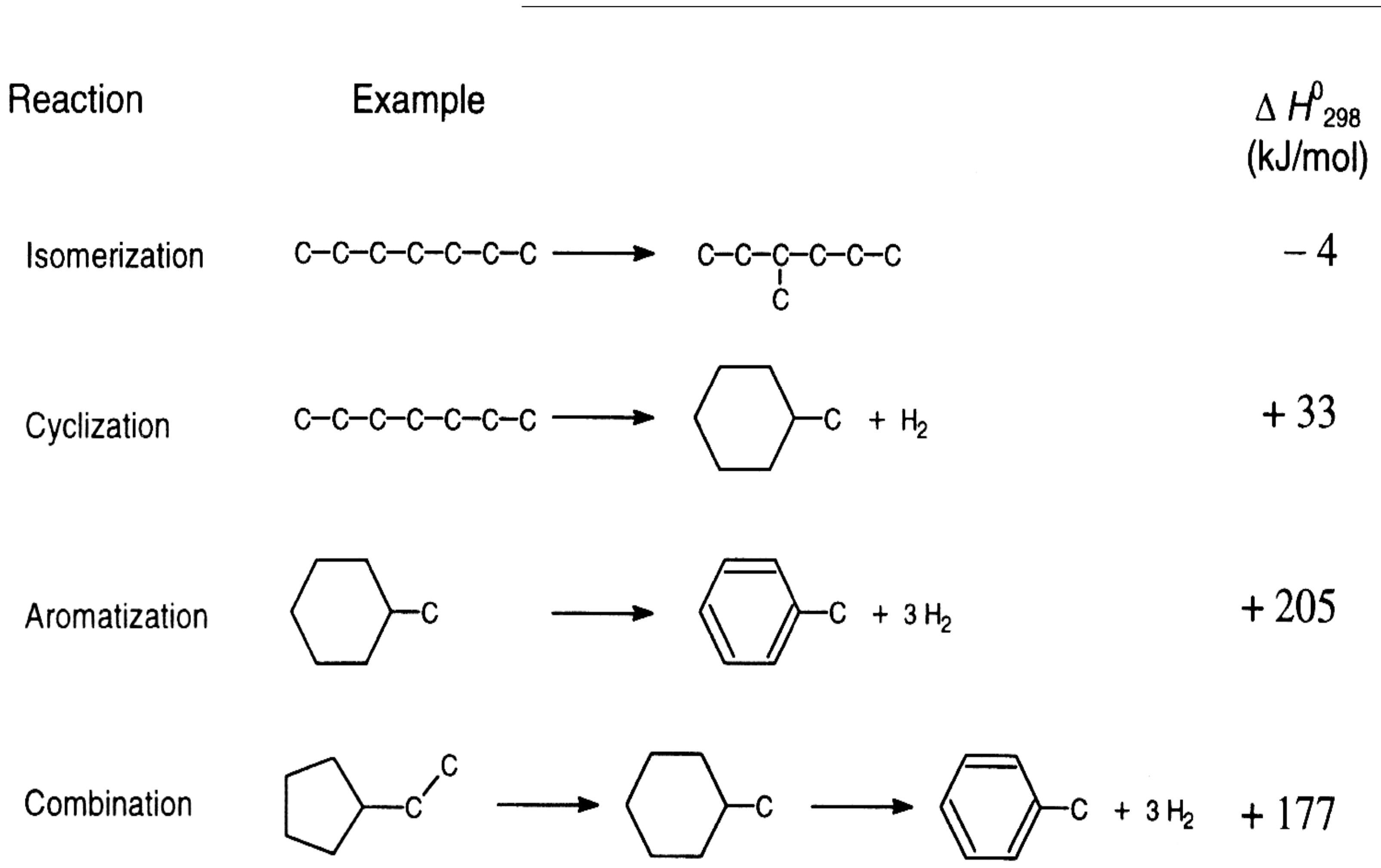
Hydrocracking Flow Scheme



Catalytic Reforming

- Catalytic reforming is an important process used to **convert low-octane naphthas into high-octane gasoline** blending components called **reformates**.
- Reforming represents the total effect of **numerous reactions** such as cracking, polymerization, dehydrogenation, and isomerization taking place simultaneously.
- Depending on the properties of the naphtha feedstock (as measured by the paraffin, olefin, naphthene, and aromatic content) and catalysts used, reformates can be produced with very high concentrations of benzene, toluene, xylene, (BTX) and other aromatics useful in gasoline blending and petrochemical processing.
- Hydrogen, a significant by-product, is separated from the reformate for recycling and use in other processes.

Catalytic Reforming



Scheme 3.4 Reactions occurring during catalytic reforming.

Catalytic Reforming

- Most processes use **Pt as the active catalyst**. Sometimes Pt is combined with a second catalyst (bimetallic catalyst) such as rhenium.
- There are many different commercial processes including platforming, powerforming, ultraforming, and Thermofor catalytic reforming.
- Some reformers operate at **low pressure (3-13 bar**), others at **high pressures (up to 70 bar**). Some systems continuously regenerate the catalyst than in other systems. One reactor at a time is taken off-stream for catalyst regeneration

Catalytic Reforming Process

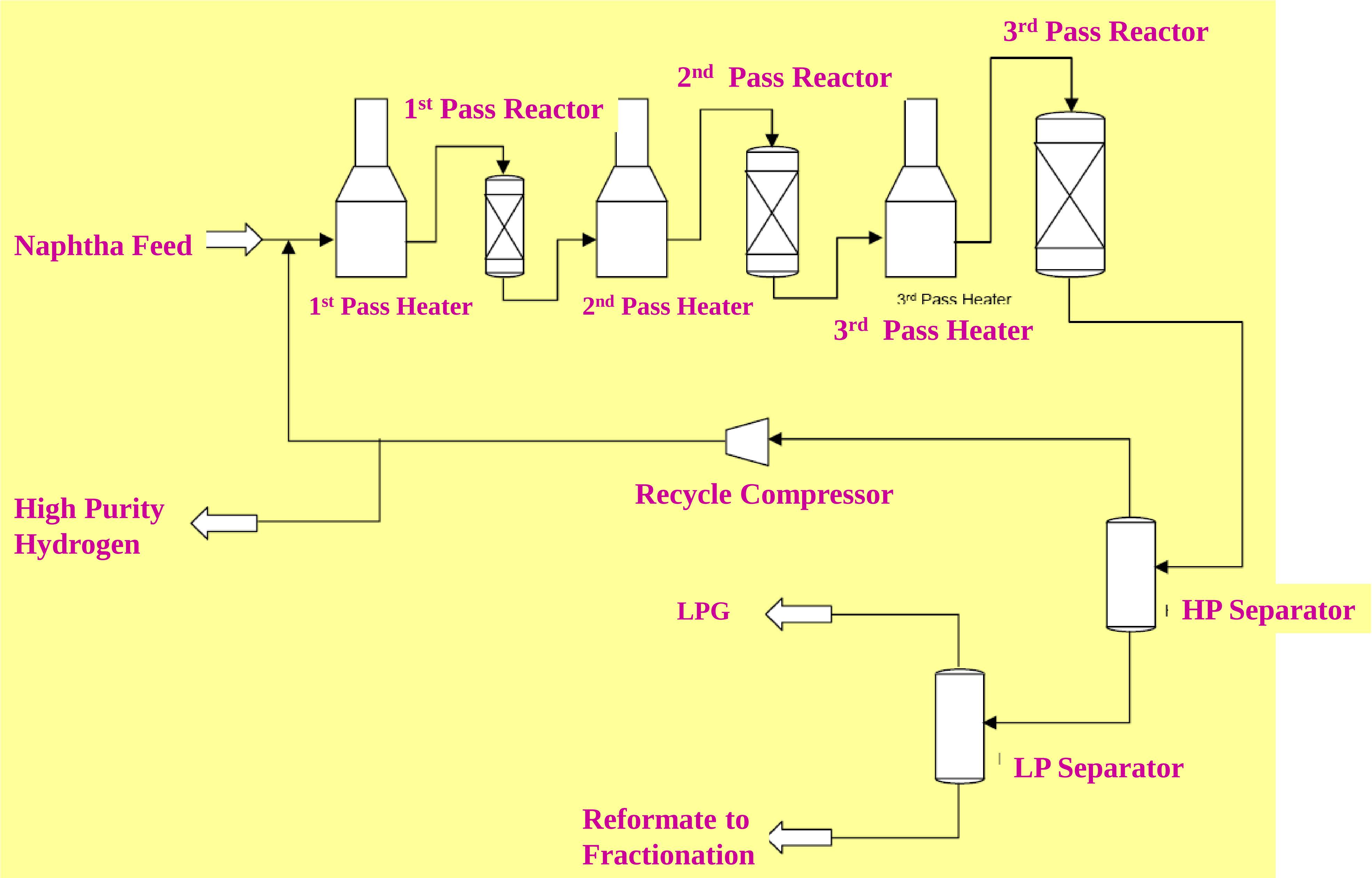
- **Process Objective:**
  - To convert low-octane naphtha into a high-octane reformate for gasoline blending and/or to provide aromatics (benzene, toluene, and xylene) for petrochemical plants. Reforming also produces high purity hydrogen for hydrotreating processes.
- **Primary Process Technique:**
  - Reforming reactions occur in chloride promoted fixed catalyst beds; or continuous catalyst regeneration (CCR) beds where the catalyst is transferred from one stage to another, through a catalyst regenerator and back again. High temperatures with typical catalysts of platinum and/or rhenium on alumina and short contact times are used
  - Desired reactions include: dehydrogenation of naphthenes to form aromatics; isomerization of naphthenes; dehydrocyclization of paraffins to form aromatics; and isomerization of paraffins.
  - Hydrocracking of paraffins is undesirable due to increased light-ends make.

Process steps:

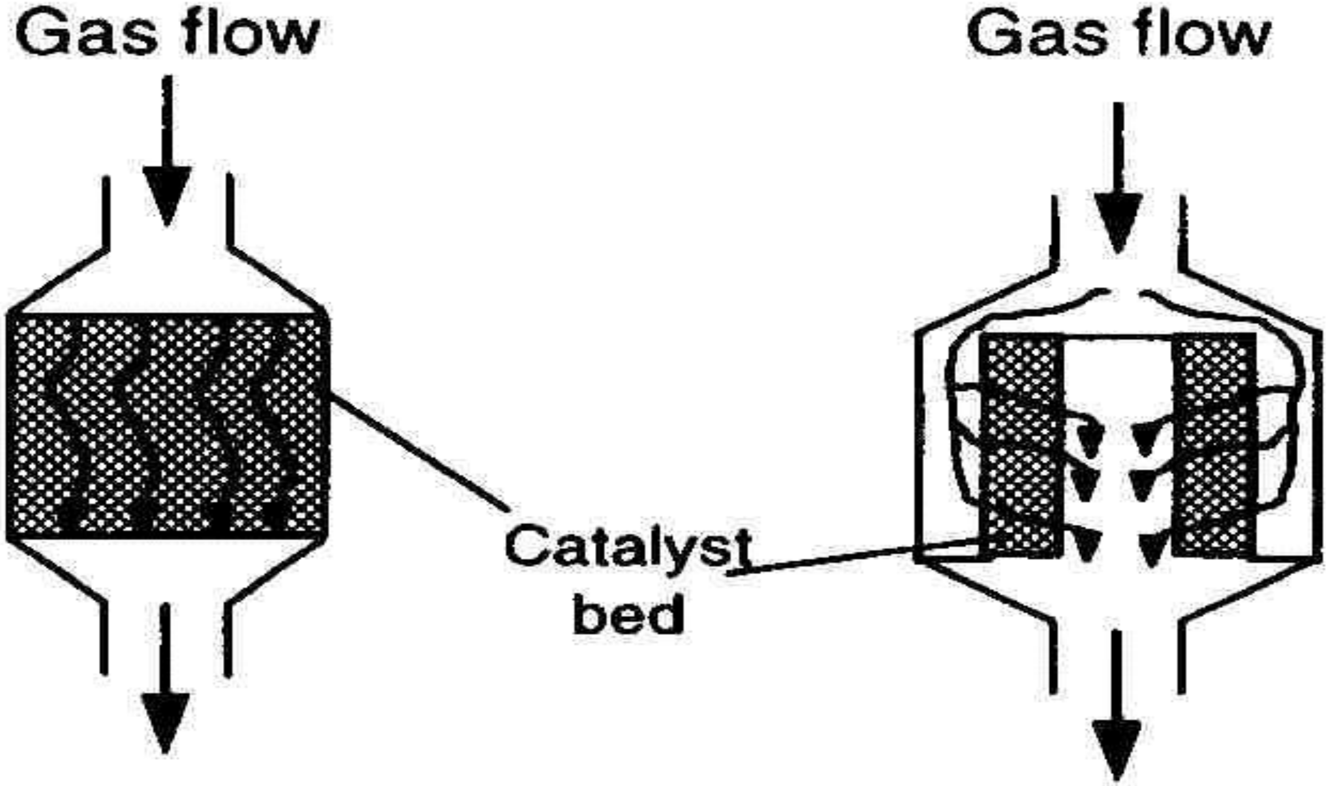
- In the platforming process, the naphtha feedstock is mixed with recycled hydrogen, vaporized , and passed through a series of alternating furnace and fixed-bed reactors containing a platinum catalyst.
- Each pass requires heat input to drive the reactions

- The effluent from the last reactor is cooled and sent to a separator to permit removal of the hydrogen-rich gas stream from the top of the separator for recycling.
- The liquid product from the bottom of the separator is sent to a fractionator called a stabilizer (**butanizer**). It makes a bottom product called reformate; butanes and lighter go overhead and are sent to the saturated gas plant.

Catalytic Reforming/ Process Schematic



Catalytic reforming reactors



Axial-flow reactor

Radial-flow reactor

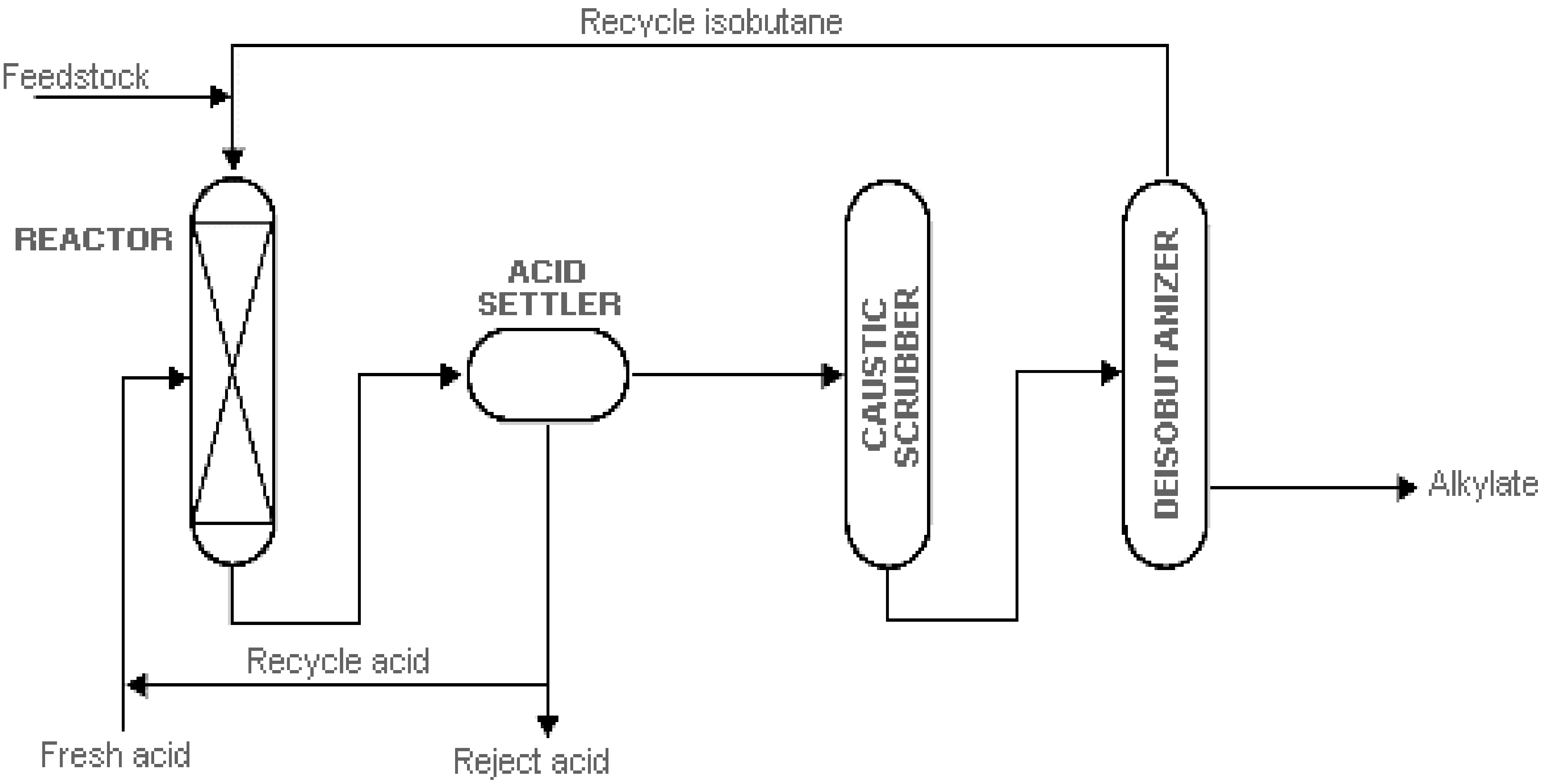
Alkylation

- Alkylation combines low-molecular-weight olefins (primarily a mixture of propylene and butylene) with **isobutene** in the presence of a catalyst, either **sulfuric acid or hydrofluoric acid**.
- The product is called **alkylate (gasoline)** and is composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons.
- **Alkylate** is a premium blending stock because it has exceptional antiknock properties and is clean burning. The octane number of the alkylate depends mainly upon the kind of olefins used and upon operating conditions.

Sulphuric acid alkylation process

- In cascade type sulfuric acid (H_2SO_4) alkylation units, the **feedstock (propylene, butylene, amylene, and fresh isobutane)** enters the reactor and contacts the concentrated sulfuric acid catalyst (in concentrations of 85% to 95% for good operation and to minimize corrosion).
- The reactor is divided into zones, with olefins fed through distributors to each zone, and the sulfuric acid and isobutanes flowing over baffles from zone to zone.
- The reactor effluent is **separated into hydrocarbon and acid phases** in a settler, and the acid is returned to the reactor.
- The hydrocarbon phase is hot-water washed with caustic for pH control before being successively depropanized, deisobutanized, and debutanized.
- The alkylate obtained from the deisobutanizer can then go directly to motor-fuel blending or be re-run to produce aviation-grade blending stock. The **isobutane is recycled** to the feed.

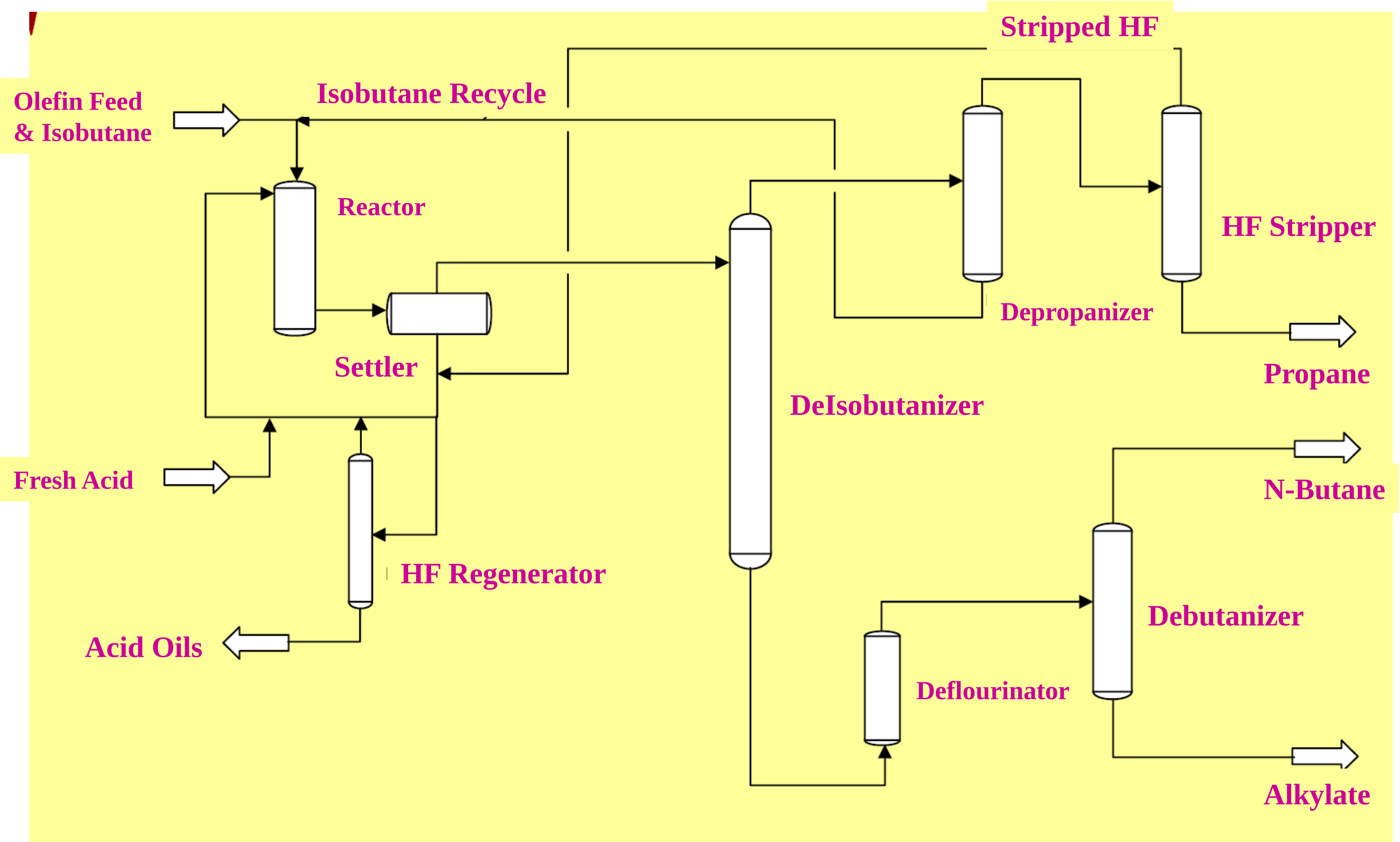
Sulphuric acid alkylation process



HF Alkylation Process

- **Process Objective:**
  - To combine light olefins (propylene and butylene) with isobutane to form a high octane gasoline (alkylate).
- **Primary Process Technique:**
  - Alkylation occurs in the presence of a highly acidic catalyst (hydroflouric acid or sulfuric acid).
- **Process steps:**
  - Olefins from FCC are combined with Iso-Butane and fed to the HF Reactor where alkylation occurs
  - Acid settler separates the free HF from the hydrocarbons and recycles the acid back to the reactor
  - A portion of the HF is regenerated to remove acid oils formed by feed contaminants or hydrocarbon polymerization
  - Hydrocarbons from settler go to the De-Isobutanizer for fractionating the propane and isobutane from the n-butane and alkylate
  - Propane is then fractionated from the isobutane; propane as a product and the isobutane to be recycled to the reactor
  - N-Butane and alkylate are deflourinated in a bed of solid adsorbent and fractionated as separate products

HF Alkylation/ Process Schematic



TREATMENT OF REFINERY GASES

- Removal of H_2S from gases is usually performed by absorption in the liquid phase.
- The concentrated H_2S is frequently converted to elemental sulphur by the “Claus” process.
- In the Claus process 95-97% of the H_2S is converted.
- H_2S is often removed with solvents that can be regenerated, usually alkanolamines: *e.g.* $CH_2(OH)CH_2NH_2$ MEA (mono-ethanolamine).
- These amines are highly water soluble with low volatility and their reaction with H_2S is much faster than with CO_2 so that the amount of absorbed CO_2 can be limited by selecting appropriate conditions.