Chapter 3

Fractionation of Petroleum

Topics

- Introduction
- Physical & Chemical Processes
- Pretreatment
  - Dehydration & Desalting of Crudes
- Distillation of petroleum
  - Atmospheric Distillation Unit(ADU)
  - Vacuum Distillation Unit(VDU)
- Arrangements of Towers
  - Top tray reflux tower
  - Pump back reflux tower
  - Pump around reflux tower

Refining operations

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

1. Fractionation (distillation)

- 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.
  - 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.

4. Formulating and Blending

- This is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties.

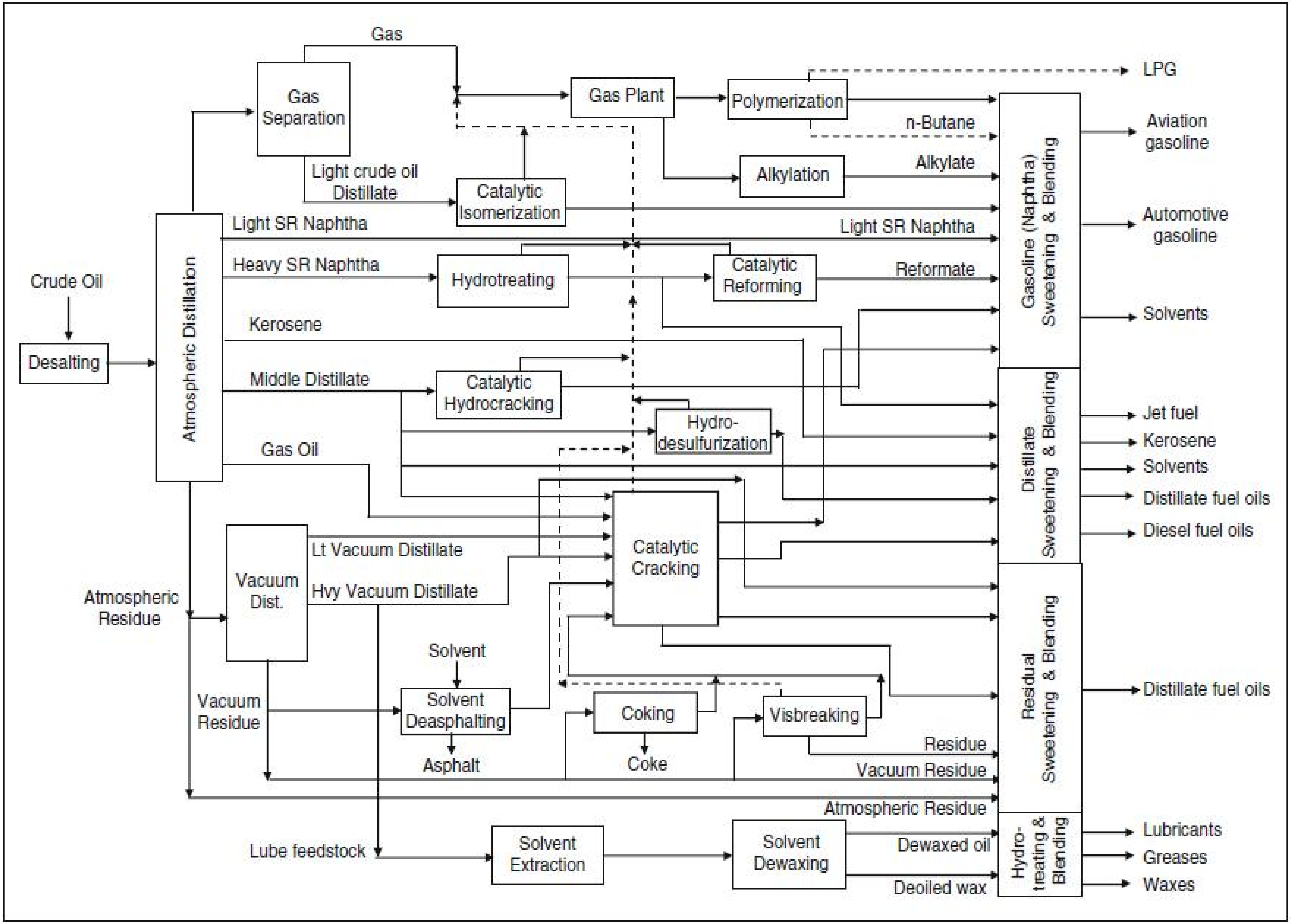
5. Environmental protection processes or Other Refining Operations :

- 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.

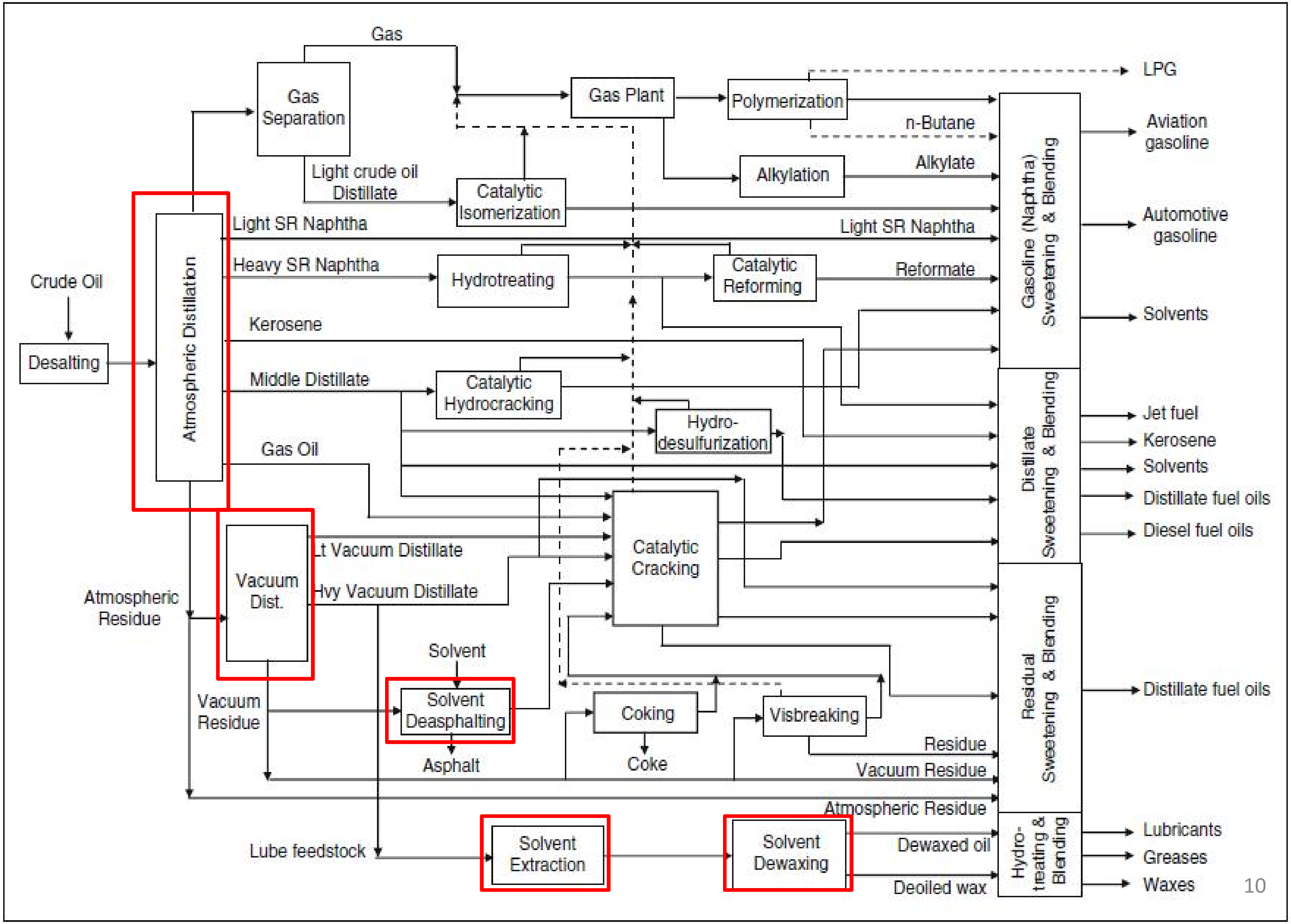
Physical and chemical processes

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

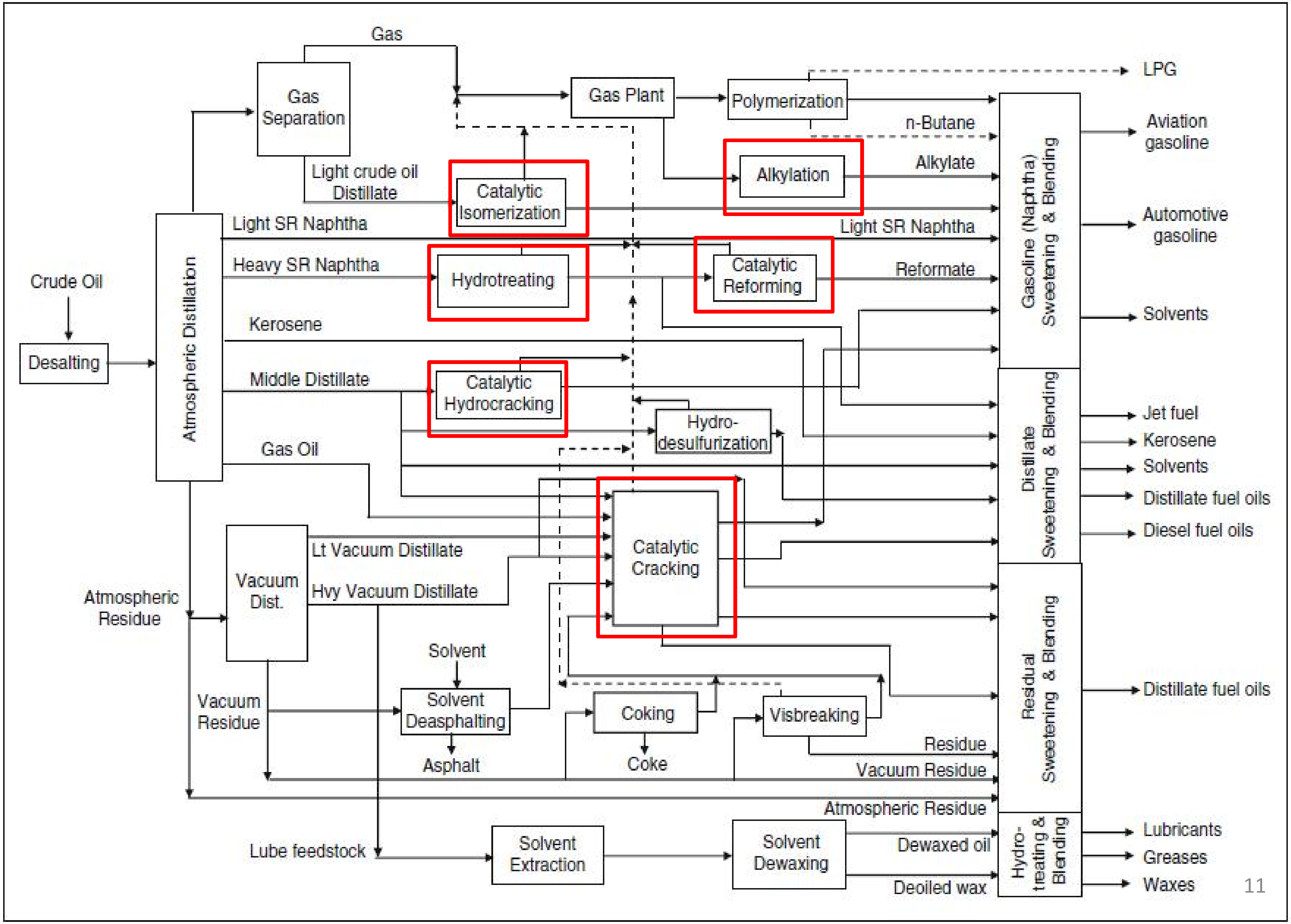
Refinery-petrochemical integration


Gas
LPG
Gas Separation
Gas Plant
Polymerization
n-Butane
Aviation gasoline
Light crude oil Distillate
Alkylation
Alkylate
Catalytic Isomerization
Automotive gasoline
Light SR Naphtha
Light SR Naphtha
Crude Oil
Heavy SR Naphtha
Hydrotreating
Catalytic Reforming
Reformate
Gasoline (Naphtha) Sweetening & Blending
Solvents
Desalting
Atmospheric Distillation
Kerosene
Middle Distillate
Catalytic Hydrocracking
Hydro-desulfurization
Jet fuel
Kerosene
Solvents
Gas Oil
Distillate Sweetening & Blending
Distillate fuel oils
Diesel fuel oils
Vacuum Dist.
Lt Vacuum Distillate
Catalytic Cracking
Hvy Vacuum Distillate
Atmospheric Residue
Solvent
Residual Sweetening & Blending
Distillate fuel oils
Vacuum Residue
Solvent Deasphalting
Coking
Visbreaking
Asphalt
Coke
Residue
Vacuum Residue
Atmospheric Residue
Lube feedstock
Solvent Extraction
Solvent Dewaxing
Dewaxed oil
Deoiled wax
Hydro-treating & Blending
Lubricants
Greases
Waxes

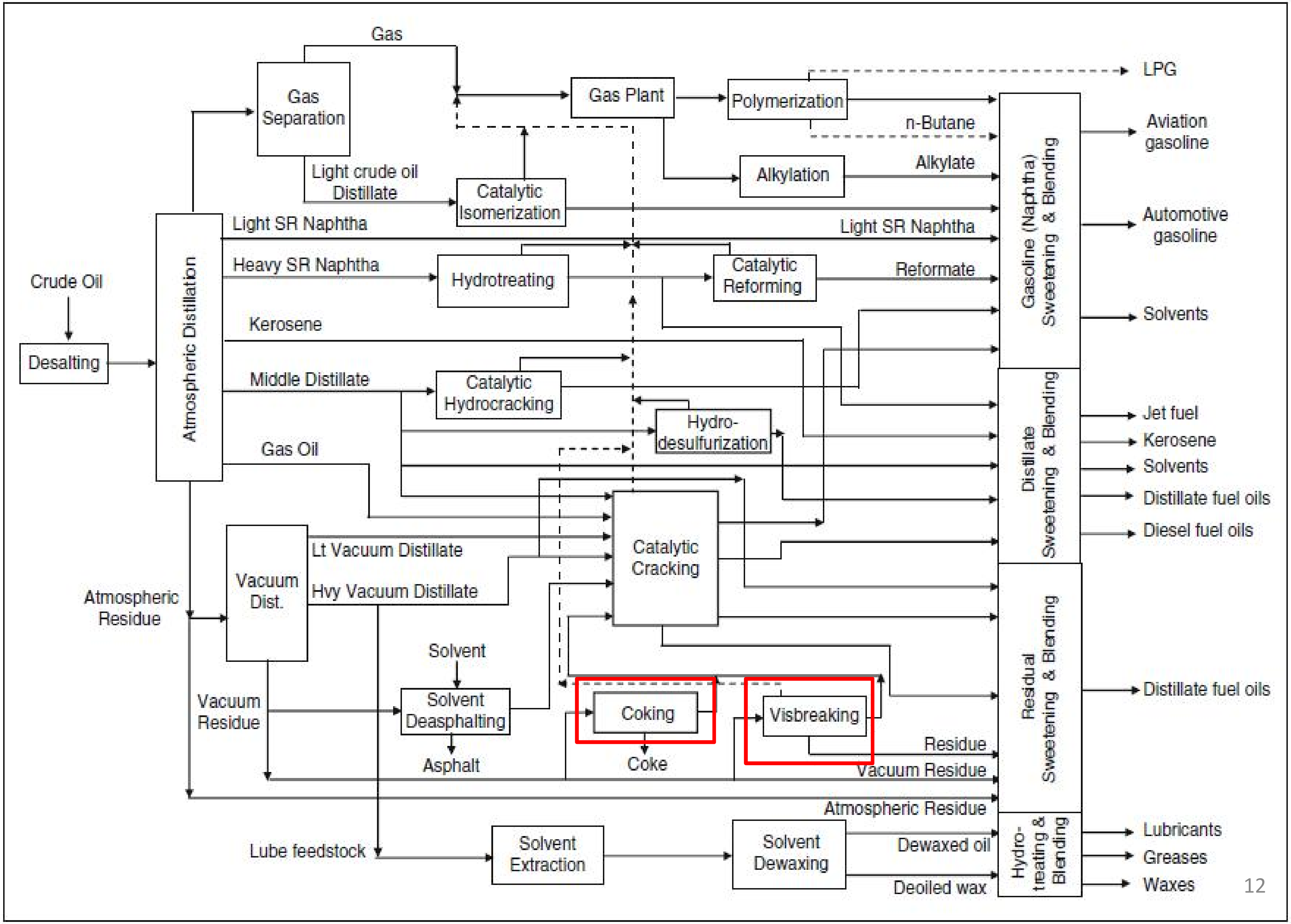
Physical Separation Processes



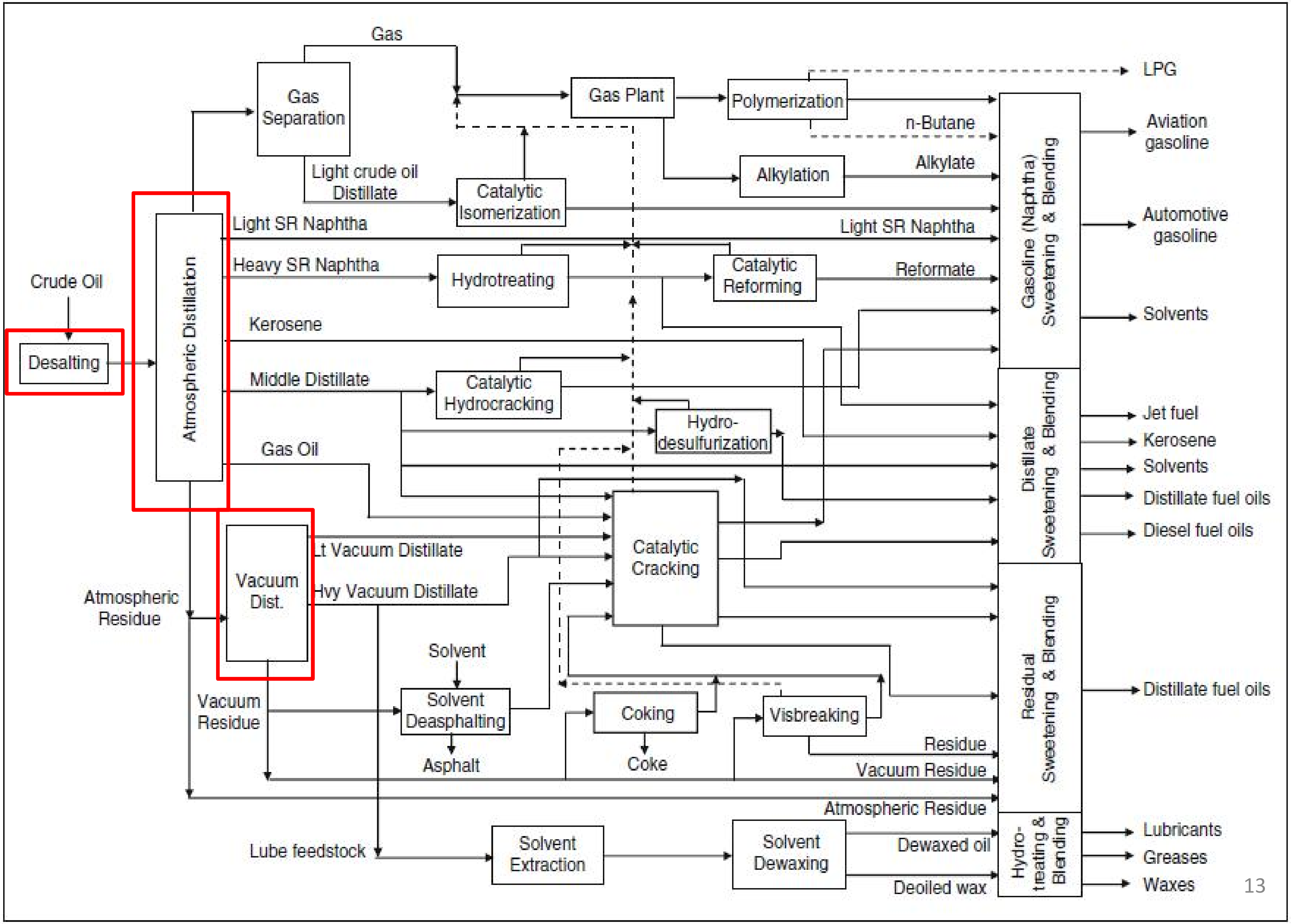
Chemical Catalytic Conversion Processes



Thermal Chemical Conversion Processes



Physical Separation Processes



Physical Separation processes

- Separating the components of crude oil without changing the chemical nature.
- Separation is based on the differences of certain physical properties of the constituents. e.g. boiling points, melting points, ..etc.
  - Desalting Unit
  - Atmospheric Distillation Unit(ADU)
  - Vacuum Distillation Unit(VDU)

Pre-treatment

Dehydration and desalting of crude

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

Pre-treatment

Dehydration and desalting of crude

- As a first step in the refining process, to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning the catalysts in processing units, these contaminants must be removed by desalting (& dehydration).
- Operation aims to completely eliminate the water that appears in the fluid forming stable emulsions, and the removal of water-soluble inorganic salts associated with the water.

Pre-treatment

Dehydration and desalting of crude

- Water is likely to occur in emulsion form when the crude are naphthenic or sulfurous
  - No harm may be expected to the distillation column due to the presence of moisture , as there is always steam in distillation.
- Crude has to be dehydrated to remove the salts.

Methods for dehydration of crudes

- Following methods are versatile for dehydration of crudes.
  - Chemical treatment
  - Gravity settling
  - Centrifugal separation
  - Electric desalter

Pre-treatment
Dehydration and desalting of crude

- Dehydration of crude is practiced in two stages, first in the site and later in the refinery.
- At the site (oil field) : salt is removed by 1) settling or by 2) adding chemicals or by 3) Combination of these two.
- Crude possessing emulsifying characteristics are not responsive to settling method
  - for these demand demulsifying agent to increase the coalescence of water drops.
  - Soda ash, sodium hydroxide, salt of fatty acids petroleum sulfonates which assist coalescence of water droplets.

Pre-treatment
Dehydration and desalting of crude

- A good amount of water should be available in crude for such treatment.
- After adding the chemicals and water to the desired extent the crude mixture is allowed to stand 75-80 ^{o}C at 15 kg/cm^2 in huge tall tanks.
- Demulsifying chemicals,if necessary are added in very small amounts.
- Retention time is about 48 hours.

Pre-treatment

Dehydration and desalting of crude

- Settling techniques are not efficient and time consuming, continuous operations are not possible with result large amount of space & equipment are to be isolated for this purpose.
- Centrifugal separation is also not economical due to huge energy requirements & less quantity handled.

Pre-treatment
Dehydration and desalting of crude

- Two most typical methods of crude-oil desalting, chemical and electrostatic separation, use hot water as the extraction agent.
- In chemical desalting, water and chemical surfactant (demulsifies) are added to the crude, heated so that salts and other impurities dissolve into the water or attach to the water, and then held in a tank where they settle out.

Pre-treatment
Dehydration and desalting of crude

- 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.
- Both methods of desalting are continuous.

Electric Desalting

- Simultaneous desalting & dehydration is achieved with removal of more than 90% salt in less than half hour.
- Principle: under charged electric field the polar molecules orient.
- A potential 0f 20000 to 30000 volts is applied between electrodes through which crude is passed.
- Brine collects at the bottom while crude floats above & forms a separate stream.

Electric Desalting

- Temperature : 90^0C
- Pressure : 5 to 6 Kg/cm^2
- Power consumption : 0.01 Kwhr per barrel.

Types of Salts in Crude Oil

- Salts in the crude oil are mostly in the form of dissolved salts in fine water droplets emulsified in the crude oil.
- Salts can also be present in the form of salts crystals suspended in the crude oil.
- These are mostly magnesium, calcium and sodium chlorides with sodium chloride being the abundant type.

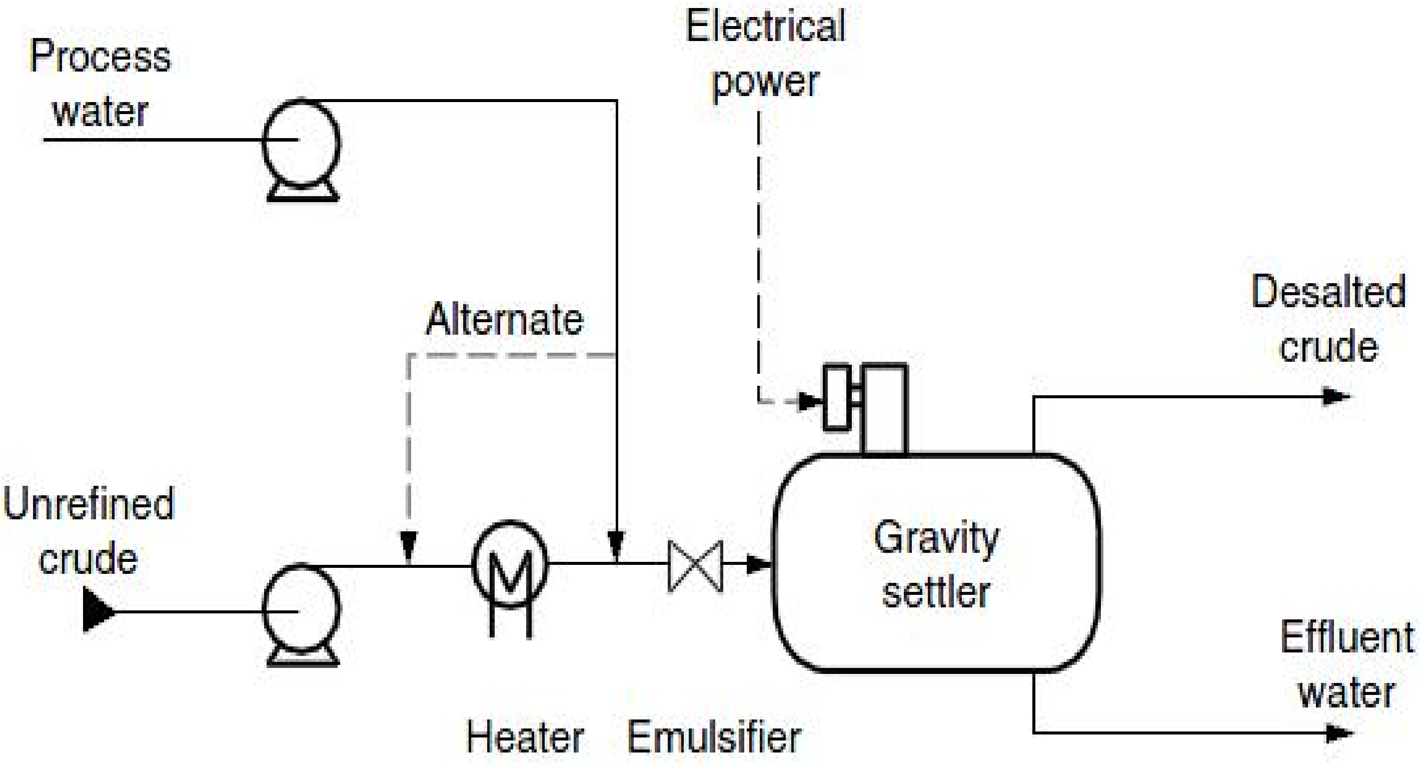
Pre-treatment
Dehydration and desalting of crude

- Of all of the existing salts, chlorides of calcium and magnesium distinguish themselves in playing an invincible role in overhead corrosion.
- These salts in presence of steam at 150-200 ^{0}C easily hydrolyze generating hydrochloric vapors. these vapors cause corrosion to equipments.
- Any crude that contains more than 5 kgs of total salts expressed in terms of sodium chloride per thousand barrels may be regarded as salty crude.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

$$CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl$$

Electrostatic desalting unit



Desalting Process

- Process is accomplished through the following steps:
- There are two types of desalting: single & multistage desalting.

1. Water washing:
   - Water is mixed with the incoming crude oil through a mixing valve.
   - Water dissolves salt crystals and the mixing distributes the salts into the water, uniformly producing very tiny droplets.
   - Demulsifying agents are added at this stage to assist in breaking the emulsion.

Desalting Process

2. Heating

- Crude oil temperature should be in the range of 49-54 ˚C (120–130^0F) since the water–oil separation is affected by the viscosity and density of the oil.

3. Coalescence

- Water droplets are so fine in diameter in the range of 1–10 mm that they do not settle by gravity.
- Coalescence produces larger drops that can be settled by gravity.
- This is accomplished through an electrostatic electric field between two electrodes.
- Electric field ionizes the water droplets and orients them so that they are attracted to each other.

Single Stage Desalting Process

- Desalter of this design achieves 90% salt removal.
- Brine collects at the bottom while crude floats above & forms a separate stream.
- Compactness, efficiency & ease of operation of these units are indubitable & brought every refinery to adopt.
- Temperature : 90^0C
- Pressure : 5 to 6 Kg/cm^2
- Power consumption : 0.01 Kwhr per barrel.

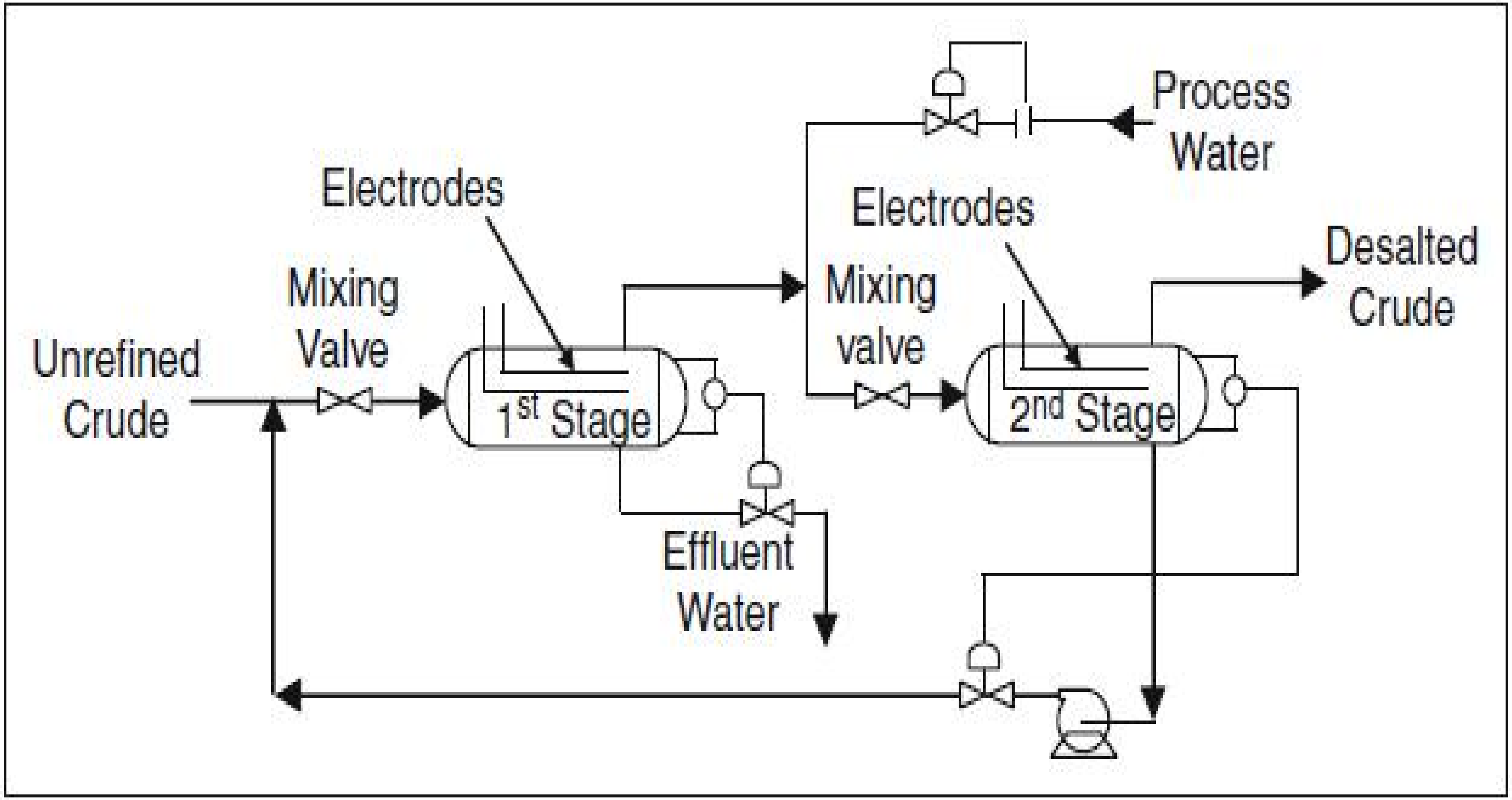
Two-stage desalting

- A high degree of salt removal is desired (95 – 99% removal of the dissolved salt in the crude oil).
- Commercial crudes, salt contents 10-200 ppb, earlier 10-20 ppb were considered satisfactorily low.
- Many refiners now aim at 5 ppb or less (1-2 ppb) which is not possible through single stage desalting, hence two stage desalting is required.

Two-stage desalting

- 99% salt removal is possible with two-stage desalters.
  - A second stage is also essential since desalter maintenance requires a lengthy amount of time to remove the dirt and sediment which settle at the bottom.
  - Crude unit can be operated with a one stage desalter while the other is cleaned.

Two-stage desalting



Desalting Operating Variables

- For an efficient desalting operation, the following variables are controlled:
- Desalting temperature: Settling rate depends on density and viscosity of crude

T ↑ density & viscosity ↓ settling rate ↑

- Desalting temperature can vary between 40 and 150 °C.
- Washing water ratio: Adding water to the crude oil helps in salt removal.

Wash water rate ↑ Coalescence rate ↑

Desalting Operating Variables

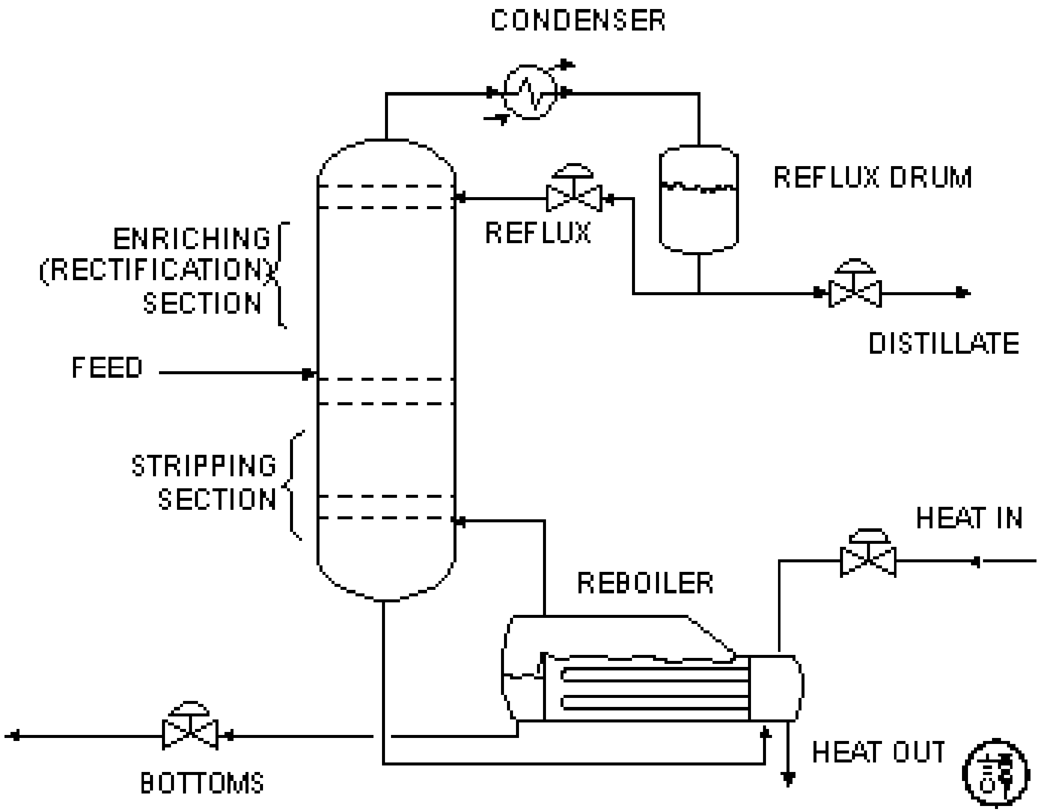
- **Water level:**
  - Raising the water level reduces the settling time for the water droplets in the crude oil.
  - However, if the water level gets too high and reaches the lower electrode, it shorts out the desalter.
  - It is better to keep the level constant for stable operation.

Effects of poor desalting

- Salts deposit inside the tubes of furnaces and on the tube bundles of heat exchangers creating fouling, thus reducing the heat transfer efficiency,
- Corrosion of overhead equipment.
- Salts carried with the products act as catalyst poisons in catalytic cracking units.

Main Components of Distillation Columns

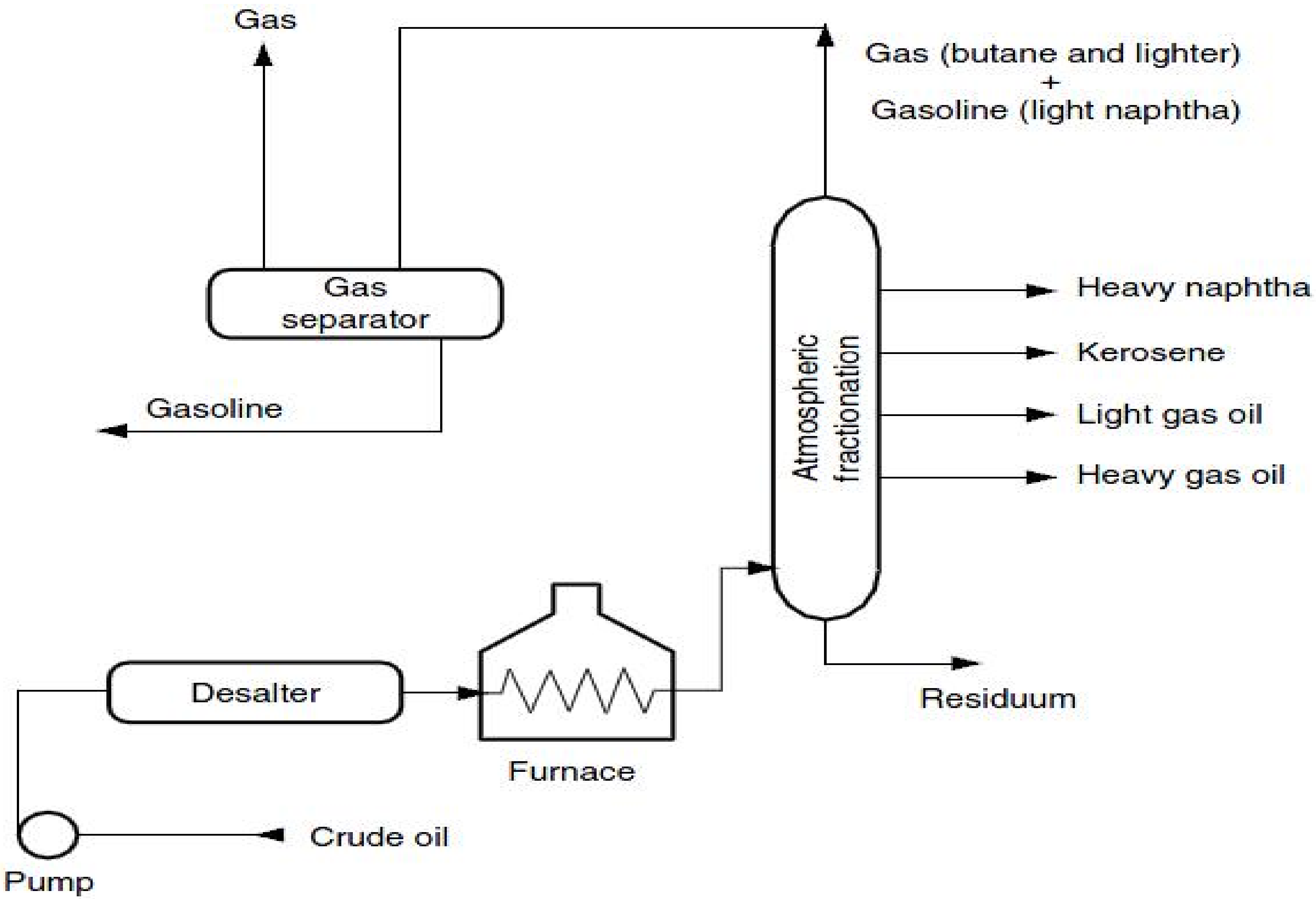
- A vertical shell where separation of liquid components is done.
- Column internals *e.g.*trays/plates and/or packings which are used to enhance component separations.
- A reboiler to provide the necessary vaporization for the distillation process.
- A condenser to cool and condense the vapour leaving the top of the column.
- A reflux drum to hold the condensed vapour from the top of the column so that liquid (reflux) can be recycled back to the column.



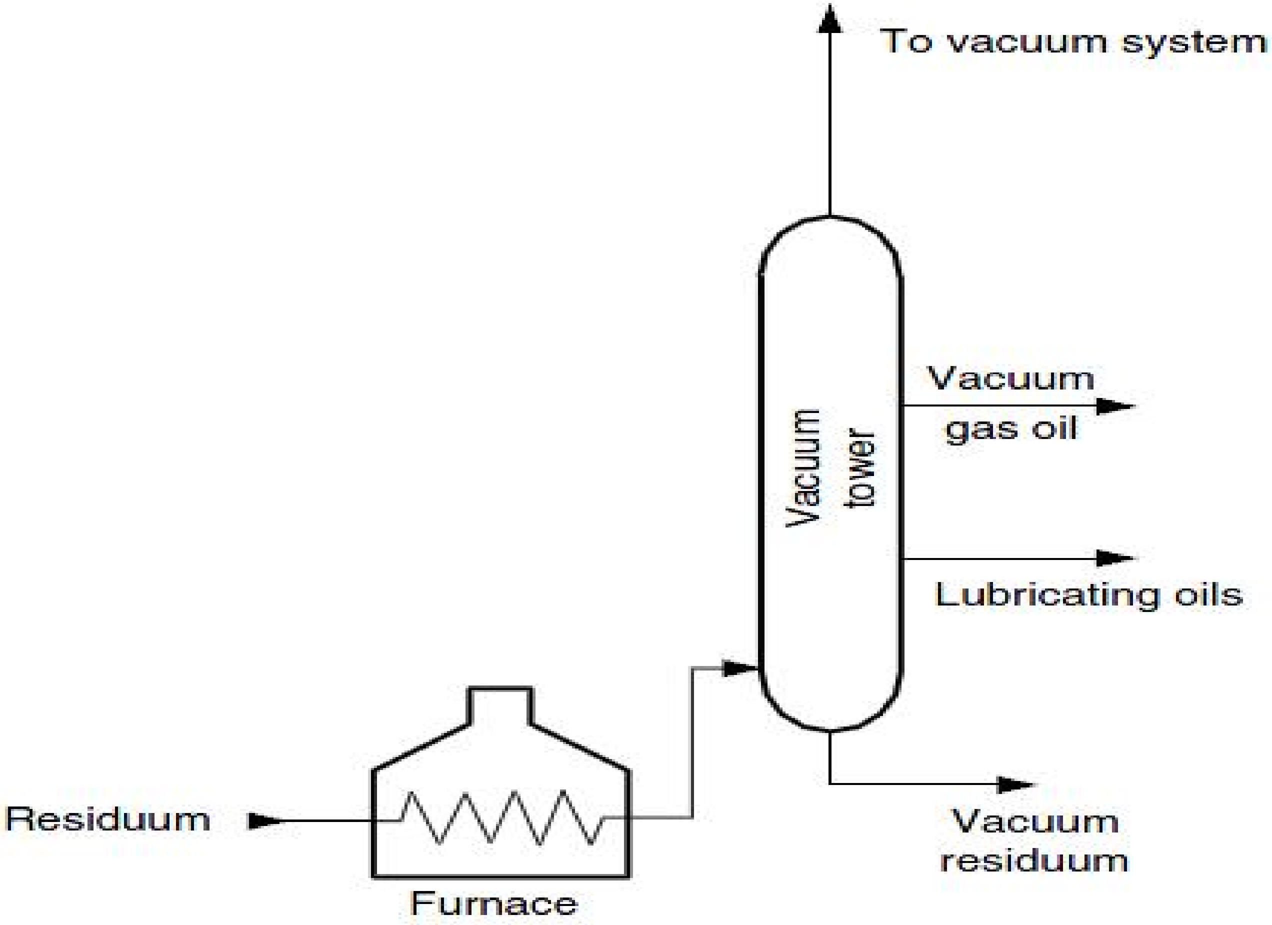
Important of stripping and Rectifying section

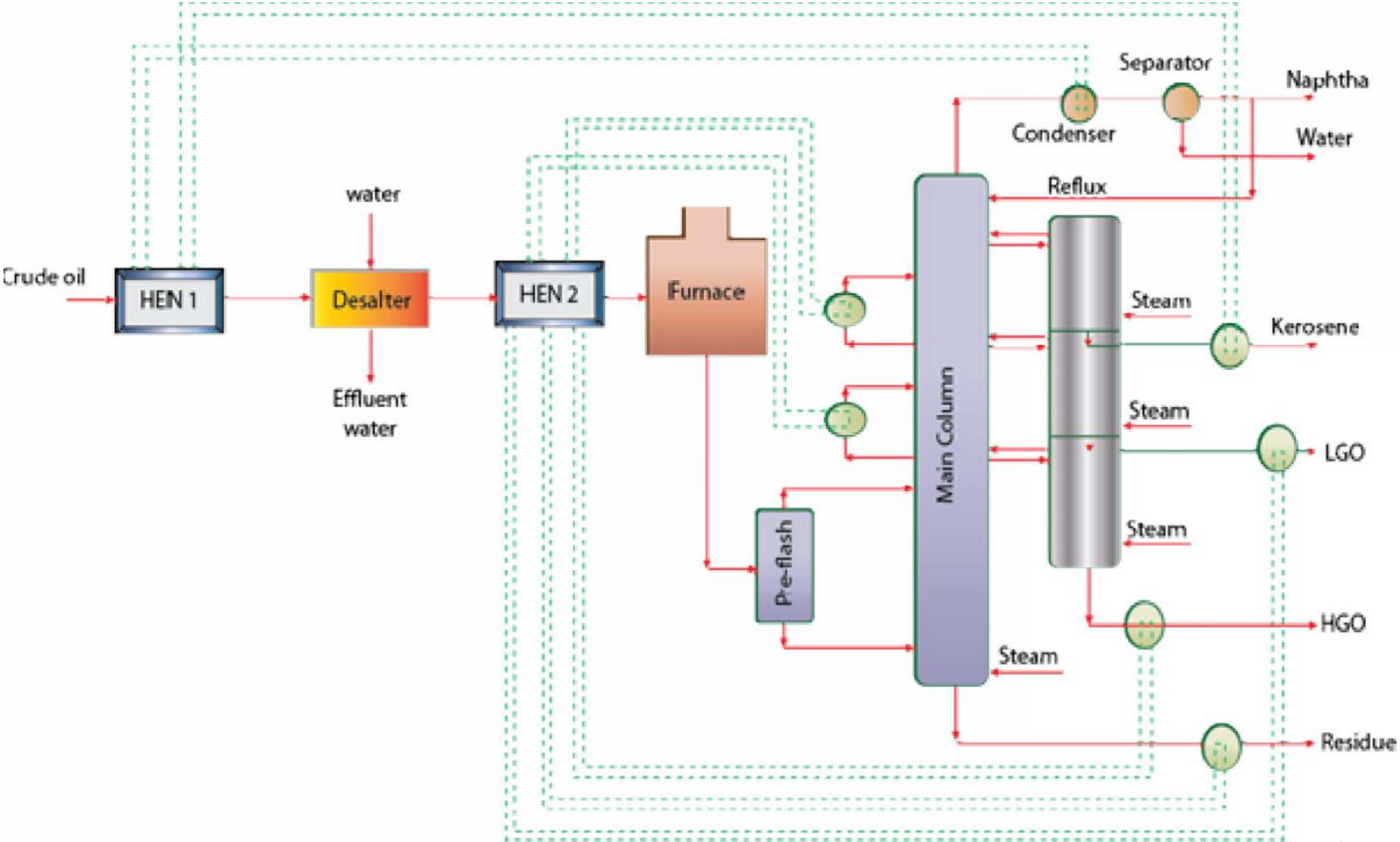
- Stripping section
  - more volatile component are stripped from the descending liquid
- Rectifying section
  - concentration of the less volatile component in the vapor is reduced

Atmospheric Distillation Unit(ADU)



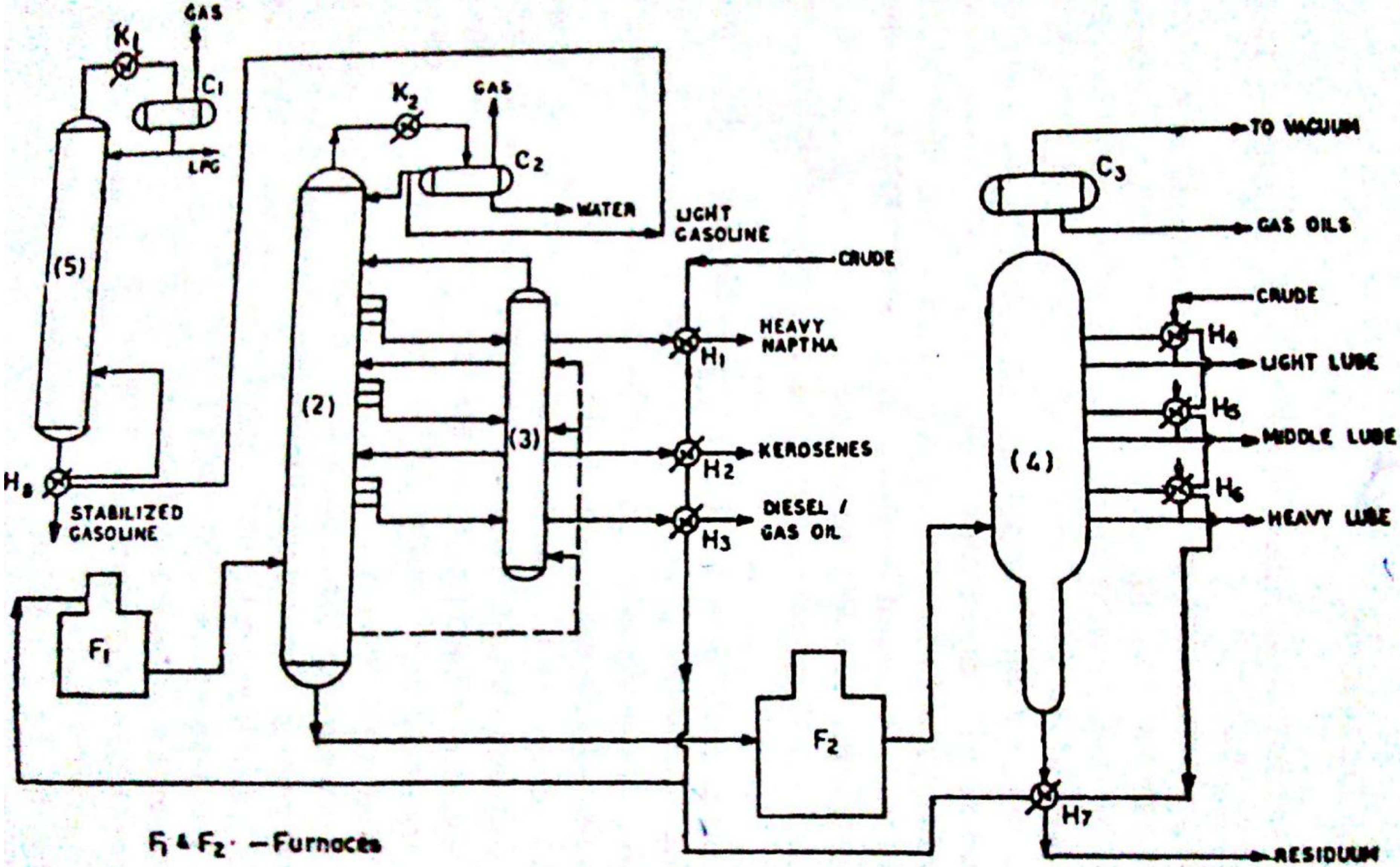
Vacuum Distillation Unit(ADU)




Crude oil
HEN 1
water
Desalter
Effluent water
HEN 2
Furnace
Pre-flash
Main Column
Condenser
Separator
Naphtha
Water
Reflux
Steam
Kerosene
Steam
LGO
Steam
HGO
Steam
Residue

Pre-flash column

- When crude contains good amount of soluble gases, to avoid load on ADU, a preflashing or topping column employed.
- Preflashing is also useful when crude has to be transported to long distance.
  - Light ends free crude gives no problem in transportation
  - A crude contains less than 6% light ends usually offers no problem in transportation.
- Preflashing is conducted at 100^0C under a pressure of 3-5 atm to remove these light ends.



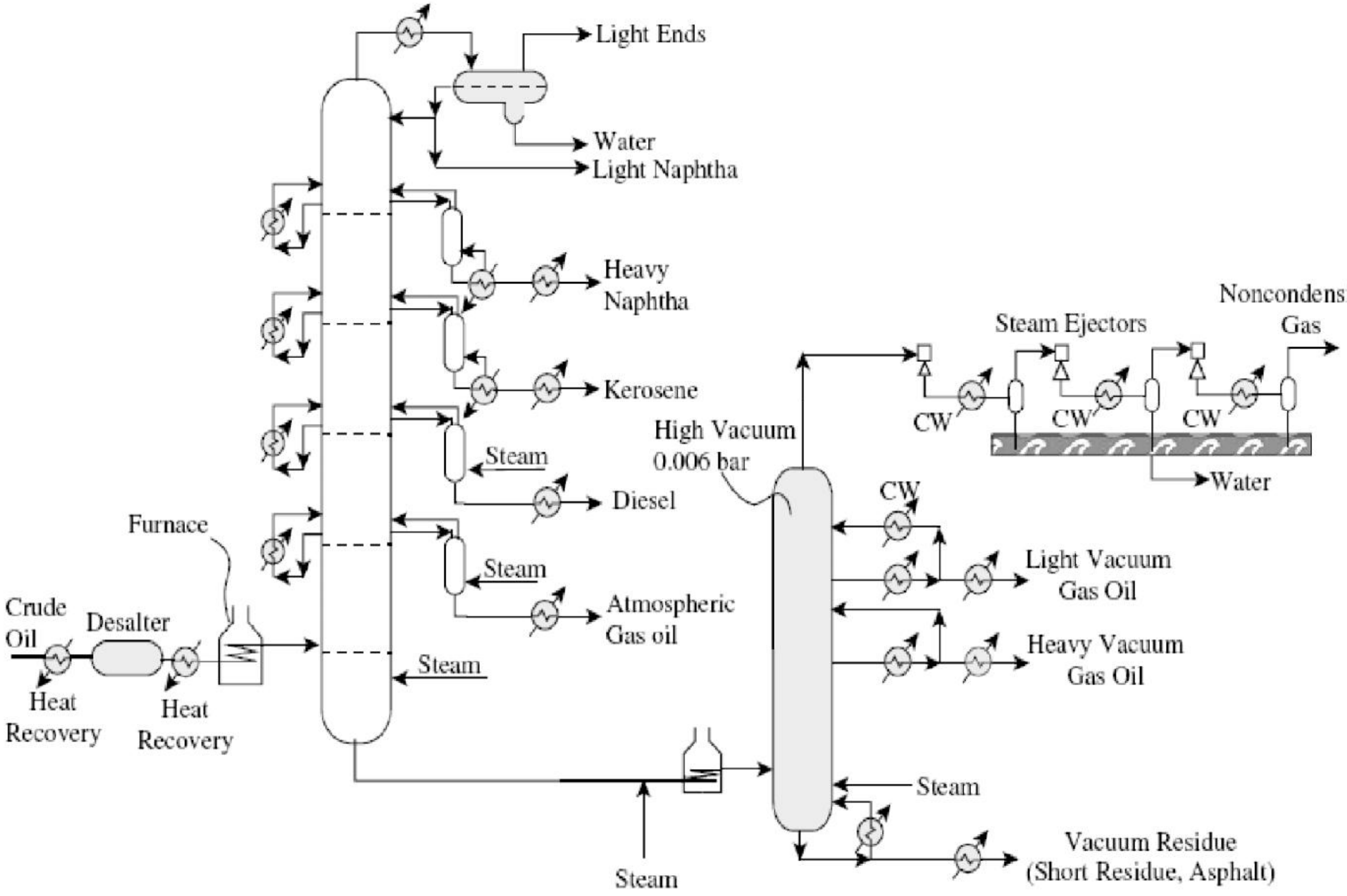
F_1 & F_2 · –Furnaces

C_1, C_2, C_3 –Reflux condensors

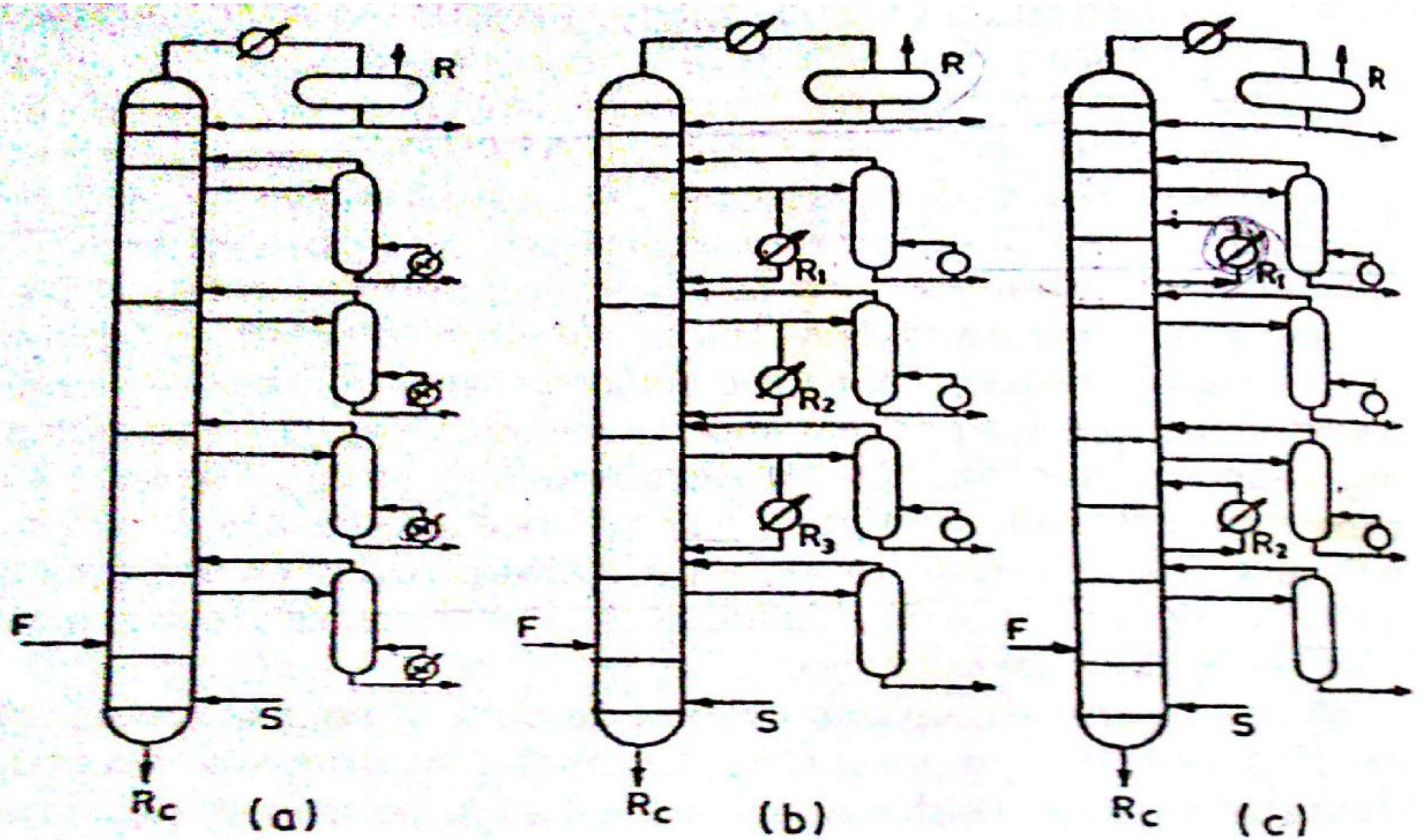
H_1……H_8 –Heat exchangers

K_1 & K_2 – Cooler

Crude Oil Distillation



Improvement of distillation efficiency



F – FEED ; S – STEAM ; R – REFLUX CONDENSER, R_1, R_2, R_3 – REFLUX
R – REDUCED CRUDE

Fig. 3.7 Arrangement of Distillation Towers
a –Top Tray Reflux, *b*–Pump Back, *c*–Pump Around Reflux.

Chapter 4

Treatment Techniques

Topics

- Introduction
- Fractions-Impurities
- Sweetening processes
- Production of LPG
- Treatment of gases
- Gasoline treatment

Treatment Processes

- Treating improves the odor, color, and stability of straight-run liquids and conversion-unit products.
- 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.
- Sulfuric acid treating removes olefins, sulfur, nitrogen, oxygen compounds, and other contaminants.
- Clay/lime treating of acid-treated oil removes any residual traces of asphaltenes.
- In the sweetening process, a light naphtha stream is washed with amine to remove hydrogen sulfide and then reacted with caustic, which promotes the conversion of mercaptans to disulfides.
- Disulfides can subsequently be extracted and removed in what is referred to as extractive sweetening.

Treatment Processes

- Purpose is to produce the required amounts of the various products from the available crude.
- Products obtained are, as a general rule, unsuitable as such for immediate use, for the following reasons :
  - Inadequate performance
  - Instability in storage ,and
  - Objectionable odor and appearance and
  - Contamination with water or particulate matter.

Fractions-Impurities

- All fractions contain impurities & classified under two headings,
  - Physical or Mechanical Impurities
    - Gases
    - Liquid fractions
  - Chemical Impurities
    - Sulfur, nitrogen & oxygen compounds are major in all fractions
    - In gaseous form sulfur is present, other than mercaptans, as hydrogen sulfide, carbonyl sulfide, carbon disulfide & sulfonil chloride.

Sweetening Processes

- Sweetening process describe the removal of hydrogen sulphide (H2S), Carbon Dioxide (CO2), and possibly other sulphur component.
- Presence of sulphur compounds like H_2S and mercaptans makes the oil sour.
- Sour stocks have bad odour.
- Processes by which the foul smelling sour petroleum products are converted into sweet smelling or odourless products are called sweetening processes.
- “Removal of sulphur compounds that cause damages is known as sweetening”.

Sweetening Processes

- Object of sweetening processes is to ensure that the finished products do not have objectionable odors.
- Objectionable odors are normally attributed to traces of mercaptans, and it is necessary either to remove them by extractive processes or by hydrodesulphurization , or to covert them into inactive disulphides.

Doctoring

- Doctor solution: A solution of sodium plumbite used to treat gasoline or other light petroleum distillates to remove mercaptan sulfur.
- Doctor test: A test used for the detection of compounds in light petroleum distillates which react with sodium plumbite.
- Doctor sweetening: A process for sweetening gasoline, solvents and kerosene by converting to disulfides using sodium plumbite & sulfur.

Doctor’s Sweetening processes

- Usually acidic sulfur can be removed by washing with any amines or caustic.
- Doctoring is principally based upon the follwing criteria.
  - Oxidising mercaptans to disulfides
    - Copper chloride sweetening process
    - Lead doctoring sweetening process
  - Physical extraction
  - In-situ destruction of sulphur bearing compounds
  - Catalytic conversions in presence of hydrogen (Catalytic desulfurization)

Merox(Mercaptan Oxidation)
Oxidising mercaptans to disulfides

- Oldest sweetening techniques involving conversion of active mercaptans to inactive disulfide.
- Disulfides in gasoline are found to be harmless compared to sulfides.
- Important sweetening reagents are chlorides & hypochlorites of copper & iron and lead dioxide and lead sulfide.

Copper chloride sweetening process

- $4CuCl_2 + 4RSH \rightarrow 2RSSR + 4HCl + 4CuCl$
- $4CuCl + 4HCl + O_2 \rightarrow 4CuCl_2 + 2H_2O$

Doctor's sweetening process(Lead doctoring process)

- Mercaptans present in the petroleum products are converted into disulphide by treatment with doctor's solution and sulphur
- $2RSH + Na_2PbO_2 \rightarrow Pb(RS)_2 + 2NaOH$
- $Pb(RS)_2 + S \rightarrow PbS + RSSR$
- $PbS + 2O_2 \rightarrow PbSO_4$
- $PbSO_4 + 4\ NaOH \rightarrow Na_2PbO2 + Na_2SO_4 + 2H_2O$

Merox(Mercaptan Oxidation)

- Mercaptans are almost removed from HC using caustic soda as the extraction solvent and converting the mercaptans into mercaptides as a result of the extraction reaction.
- Caustic is regenerated by bringing it into contact with air and catalyst to bring about oxidation of mercpatides to disulfides.
- The disulfides, insoluble in the caustic are separated from the regenerated caustic.

Merox(Mercaptan Oxidation)

- A caustic solution containing cobalt catalyst is used to convert mercaptans (RSH) to RSSR (disulphide).
- Air is used to oxidize the mercaptans to disulphides. (R-S-S-R).
- Caustic solution is then recycled for regeneration.
- It is mainly used for treatment of refinery gas streams.

Physical extraction processes

- $(HO\ CH_2\ CH_2)NH_2 + H_2S \longleftrightarrow (HO\ CH_2\ CH_2\ NH_3)_2\ S$
- $(HO\ CH_2\ CH_2)NH_2 + CO_2 + H_2O \longleftrightarrow (HO\ CH_2\ CH_2\ NH_3)_2\ CO_3$

In-situ destruction of sulfur bearing compounds

- In-situ destruction of sulfur compounds by sulfuric acid.
- Acid of above 93% strength is normally used for treatments.
- Olefins & higher unsaturates are readily attacked by sulfuric acid of 75% strength also oxygen & nitrogen compounds removed by sulfuric acid.
- In refining practice 93% acid is weakest that can be economically employed.
- $RSH + H_2SO_4 \rightarrow RSHSO_3 + H_2O$
- $RSH + RSHSO_3 \rightarrow (RS)_2SO_2 + H_2O$
- $(RS)_2SO_2 \rightarrow R_2S_2 + SO_2$

Catalytic desulphurization

- Sweetening operations are carried out by catalysts.
- Whole molecule bearing sulfur is not removed as seen in extraction or cid treatment, but only sulfur atom is picked up.
- Material loss is negligeble, with possible recovery of sulfur.

Catalytic desulphurization

- First catalytic process for removal of organic sulfur was introduced by Carpenter & Evens, using sulfides of nickel.
- Iron oxide catalysts with 5-15% Cr2O3 were used for hydrogenation & hydrolysis of carbonyl silfide from gases.
- Operate at temp. of 300-400^{0}C at 1-25 kg/cm2 pressure.
- Copper-Chromia-Alumina catalysts, Huff Catalysts promote conversion of organic sulfur compounds to H2s, which is retained in the form of metla sulfide, on catalyst.
- Cobalt,molybdenum catalysts(12-13% Co) supportes on bauxite or on fullers earth are new in this field.

Production of LPG

Introduction-LPG

- Light gas streams produced by various refinery units are collected and piped to treating plants, where:
  - Propane is recovered for LPG
  - Propylene is removed for use in petrochemical plants
  - Butanes and butenes are removed for use as alkylation feeds
  - Heavier components are recovered and sent to gasoline blending, but if necessary drying agents – alumina, silica, or molecular sieves – are used to remove the final traces of water.
  - Gases containing hydrogen sulfide are scrubbed in trayed contactors with aqueous amines such as diethanolamine (DEA).

Methods for production of LPG

- Production of LPG is mainly based upon the principle of separation.
- C3-C4 fractions can be separated from the rest of fractions by,
  - Distillation at low temperature
  - Absorption & desorption
  - Compression & expansion
  - Combined methods
- Distillation is based upon the boiling points or relative volatility while absorption is connected with selective absorption capacity of oils for certain fractions.
- Absorption method is most convincing.

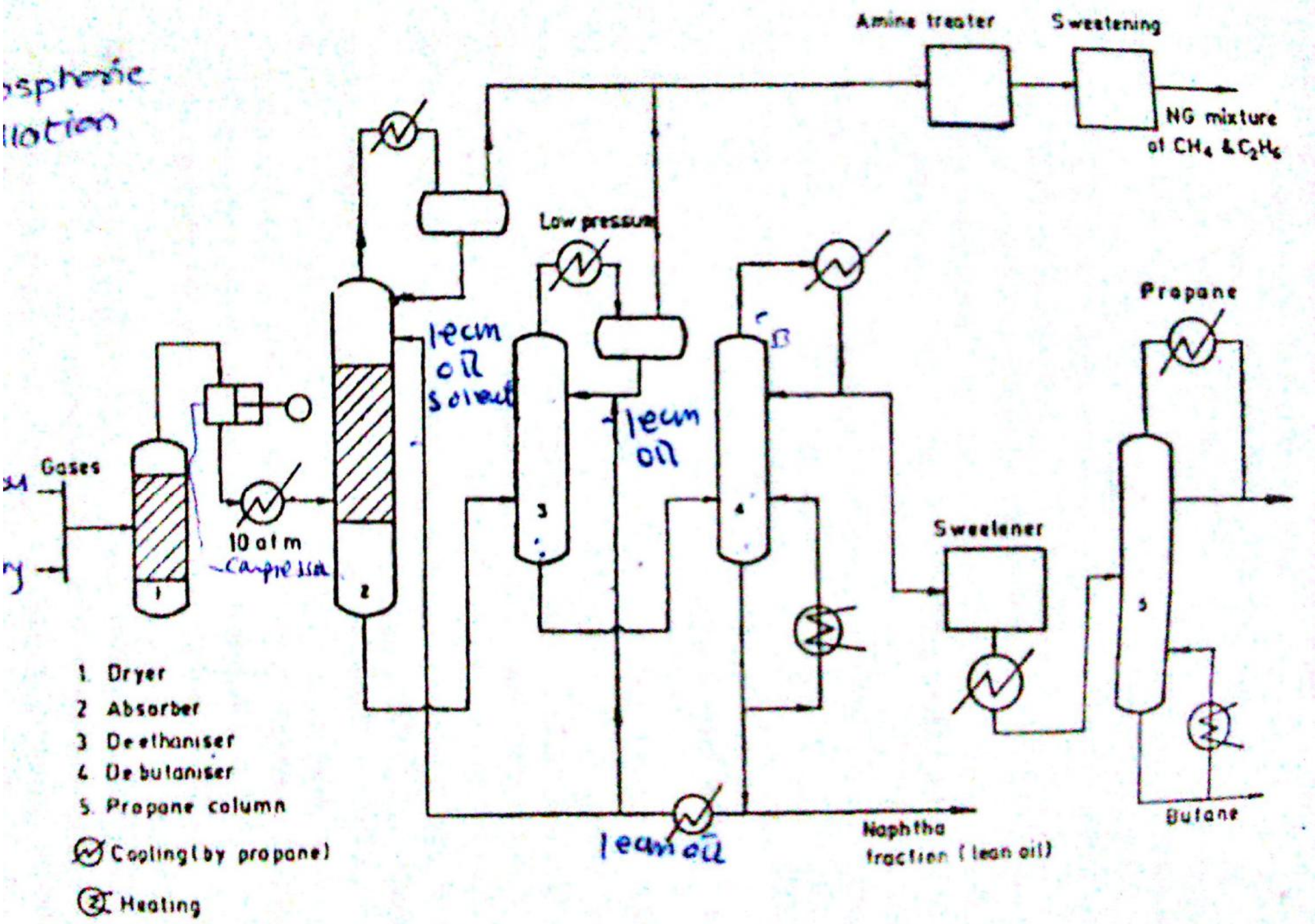


Fig. 4.1*a* LPG Production by Absorption Technique.

LPG production by Absorption Technique

- Propane, butane mixture is sold as LPG, part of butane is always reserved for bleding with gasoline.
- Oil absorption gives very pure hydrocarbons.
- A purity of 98% for propane & 95% for butane at a recovery of 70-80% is reported.
- If cracked gases contain much unsaturates, propane separation is done by other techniques, one such being low temperature fractionation.
- Low temperature fractionation is employed, when purity of products is very much essential like polymer grades, ethylene, propylene etc. and quantity of gases handles is also very much.

Amine Treatment of LPG

Acid gas removal process

- Acid gases present in LPG
  - CO_2
  - H_2S
- Gas with out CO_2 & H_2S is called "Sweet" otherwise "Sour".
- Both gases are undesirable because they cause
  - Corrosion
  - Reduce heating value
  - Reduce sale value

Acid gas removal process

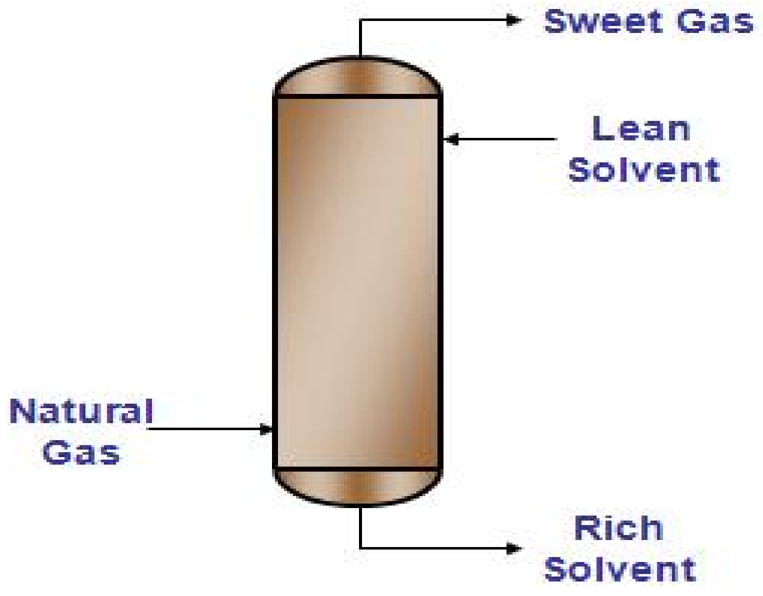
- Effects of sour gas
  - Hydrogen Sulfide
    - Toxic & Flammable gas
    - foul smelling
    - Corrosive
    - traces of it may seriously contaminate regenerative treating solvents
    - It may accumulate in dangerous concentrations in drains, valves, vessels and tanks.
  - Carbon dioxide
    - Corrosive material
    - Reduce the heating value
    - Non-combustible component

Methods for Amine treating gas

- Two processes for amine treating of gas
    - Absorption
    - Adsorption
- Processes that use aqueous solutions of various amines to remove hydrogen sulfide (H_2S), mercaptans and/or carbon dioxide (CO_2) from gases through absorption and chemical reaction.

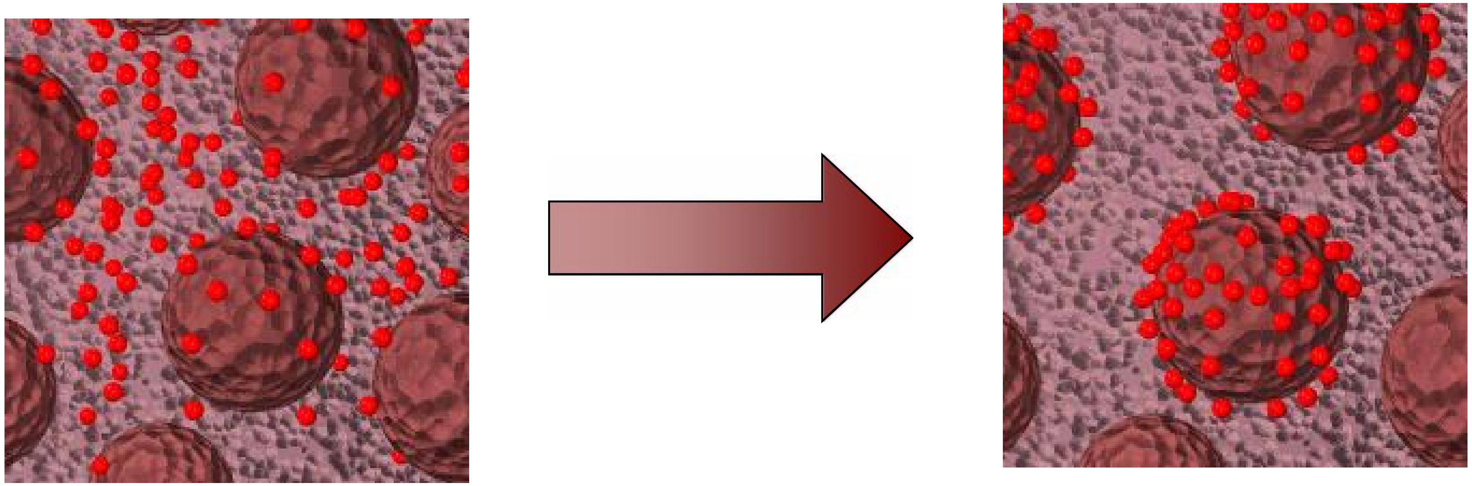
Absorption process

- It is used to remove a component (solute) from the gas stream by contacting the gas with a liquid solution (solvent).



Adsorption

- It is the process of removing impurities from a gas stream by means of a solid material called adsorbent that has special attraction for the impurities.



Absorption process by Amine solution

Chemical Solvent Process

- Chemical Solvent Process use an aqueous solution of a weak base to chemically react with & absorb the acid gases in the natural gas stream.
- Reactions involved are reversible by changing the system temperature or pressure, or both.
- Therefore, the aqueous base solution can be regenerated and circulated cycle.
- Majority of chemical solvent processes utilize either an amine or carbonate solution.

Absorption process by Amine solution

- Choice of solvent
  - High solubility.
  - Low volatility.
  - Easy to recovery.
  - Low viscosity.
  - Low cost.

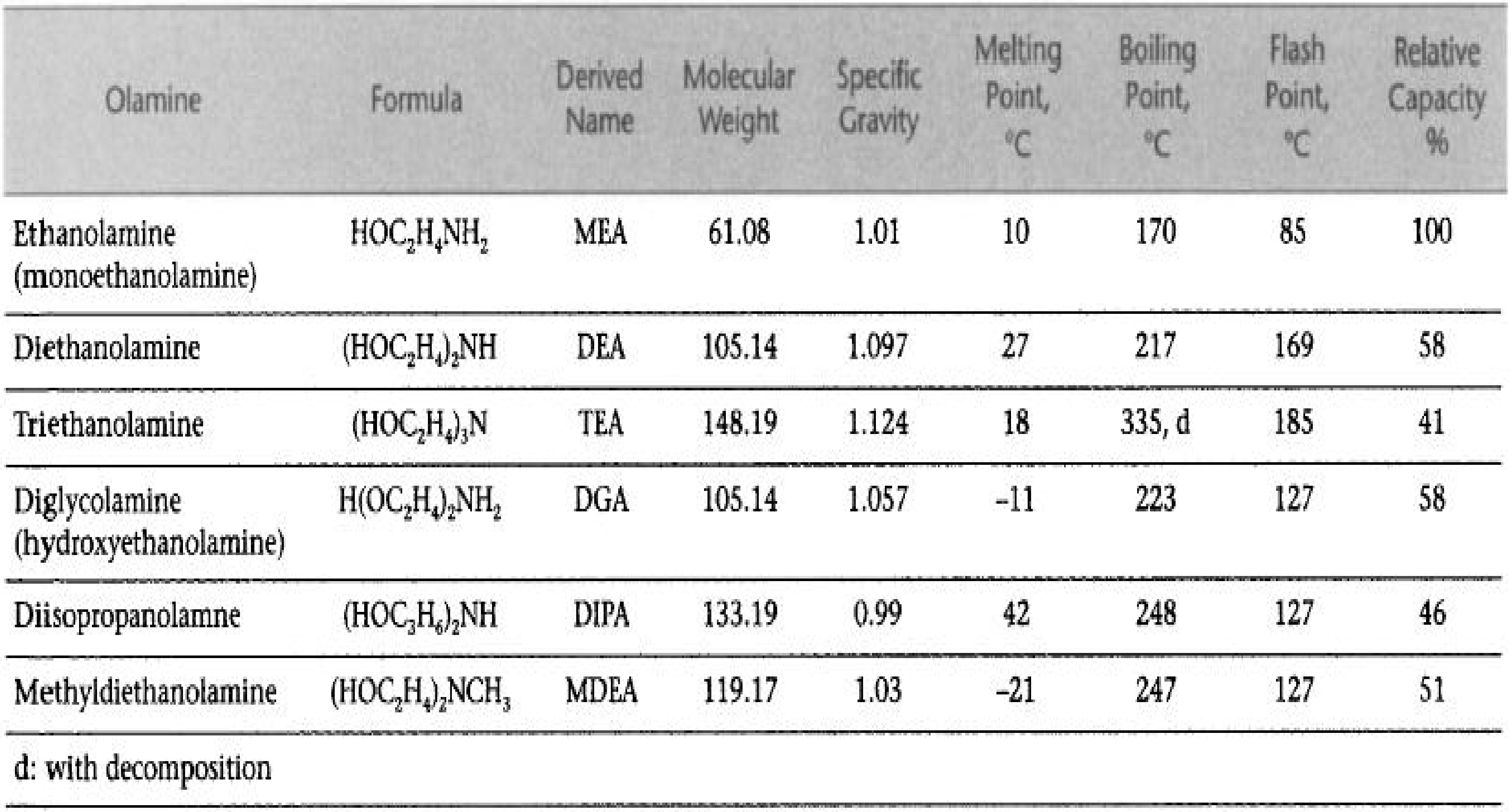
Olamines

- Amine derivatives such as
  - ethanolamine(monoethanolamine,MEA),
  - diethanolamine (DEA),
  - triethanolamine(TEA),
  - methyldiethanolamine(MDEA),
  - diisopropanolamine (DIPA), and
  - diglycolamine (DGA) are the most widely used **olamines in commercial applications.**
- They are selected according to their relative ability to interact with and remove carbon dioxide and/or hydrogen sulfide.

Ethanolamines

- Monoethanolamine (MEA) :
  - About 20 % for removing H_2S and CO_2, and about 32 % for removing only CO_2.
- Diethanolamine (DEA) :
  - About 20 to 25 % for removing H_2S and CO_2
- Methyldiethanolamine (MDEA) :
  - About 30 to 55% % for removing H_2S and CO_2
- Expressed as weight percent of pure amine in the aqueous solution.

Range of composition of NG



Olamine	Formula	Derived Name	Molecular Weight	Specific Gravity	Melting Point, °C	Boiling Point, °C	Flash Point, °C	Relative Capacity %
Ethanolamine (monoethanolamine)	$HOC_2H_4NH_2$	MEA	61.08	1.01	10	170	85	100
Diethanolamine	$(HOC_2H_4)_2NH$	DEA	105.14	1.097	27	217	169	58
Triethanolamine	$(HOC_2H_4)_3N$	TEA	148.19	1.124	18	335, d	185	41
Diglycolamine (hydroxyethanolamine)	$H(OC_2H_4)_2NH_2$	DGA	105.14	1.057	–11	223	127	58
Diisopropanolamne	$(HOC_3H_6)_2NH$	DIPA	133.19	0.99	42	248	127	46
Methyldiethanolamine	$(HOC_2H_4)_2NCH_3$	MDEA	119.17	1.03	–21	247	127	51

d: with decomposition

Monoethanolamine Systems(MEA)

- MEA is a primery amine, which has had widspread use as a gas sweetening agent.
- MEA is a stable compound and in the absence of other chemicals suffers no degradation or decomposition at temperature up to its normal boiling point.

MEA reacts with CO2 & H2S

- These reactions are reversible by changing the system temperature.
- Reactions with CO_2 & H_2S are reversed in the stripping column by heating the rich MEA to approximately 118^0C at 69 KPa(245^0F at 10 psig).
- Acid gases evolve into the vapor and are removed from the still overhead & MEA is regenerated.
- A disadvantage of MEA is that it also reacts with carbonyl sulfide(COS) and carbon disulfide(CS_2) to form heat stable salts, which cannot be regenerated at normal stripping column temperature.
- At temperature above 118^0C a side reaction with CO_2 exists which produces oxazolidone-2 , a heat stable salt, which consumes MEA from the process.

Diethanolamine Systems(DEA)

- DEA is a secondary amine also used to treat natural gas to pipeline specifications.
- As a secondary amine, DEA is less alkaline than MEA.
- DEA systems do suffer the same corrosion problems, but not as severely as those using MEA.
- Solution strength are typically from 20 to 25 percent DEA by weight in water.

Selection of solvent

- From the three types of amines, DEA amine is selected.
- Reasons for select DEA are in following points:
  - DAE is much less corrosive to carbon steel than MEA
  - DEA is less volatile then MEA

Process Description

- The gas sweetening process consists basically of two parts :

  1. Absorption   2. Regeneration

- Reaction

$$2RNH_2 + H_2S \rightarrow (RNH_3)_2S$$

$$2RHN_2 + CO_2 + H_2O \rightarrow (RNH_3)_2CO_3$$

$$\boxed{(\text{Lean DEA}) + H_2S + CO_2 \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} (\text{DEA Rich in } H_2S + CO_2)}$$

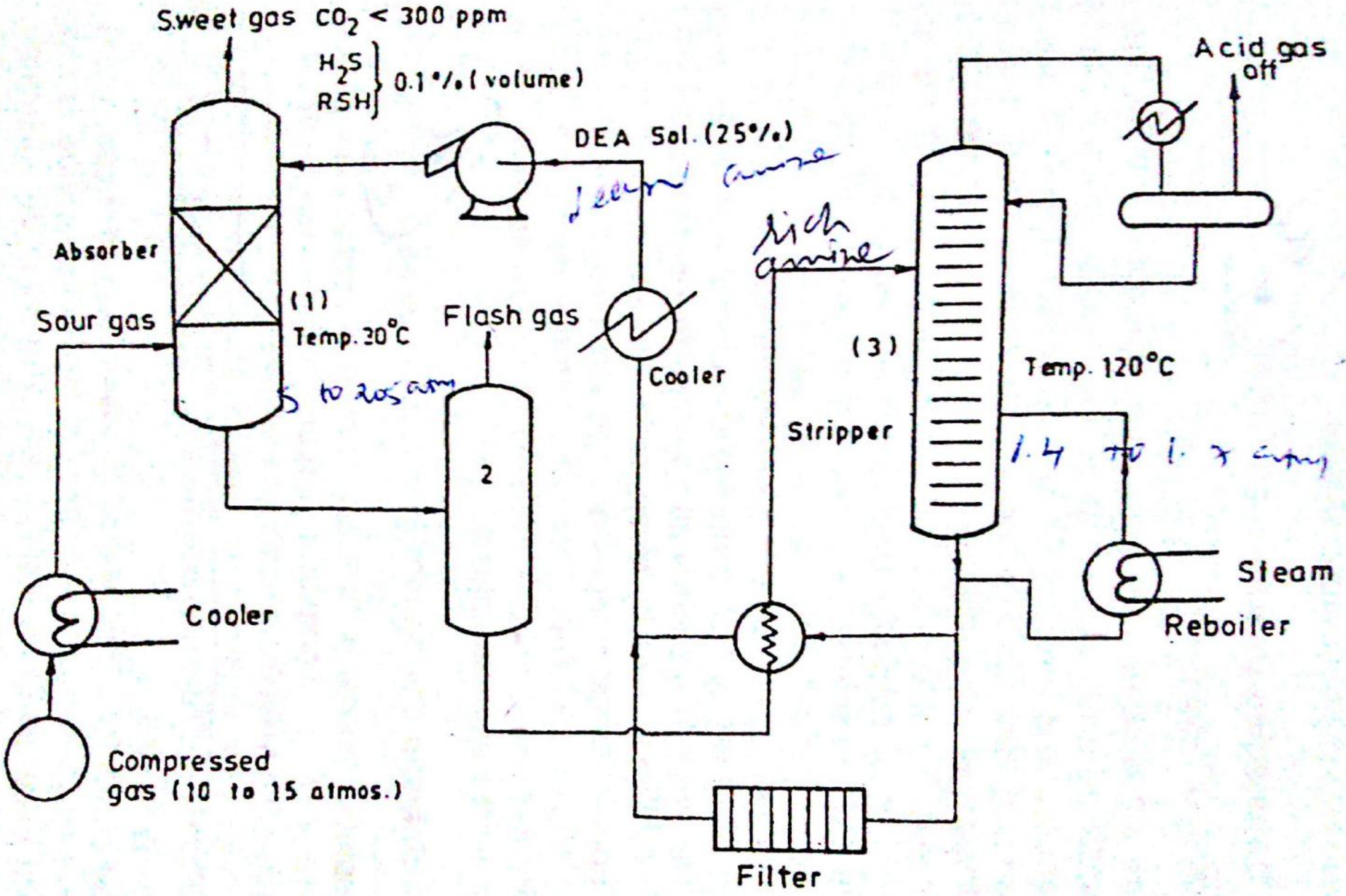


Fig. 4.2 Amine Treatment for LPG.

Acid gas purification techniques
Stretford Operation

- Stretford Process is a wet-type desulfurization process used in various industries in which hydrogen sulfide is removed from gas streams and sulfur is recovered.
- This process was developed by Tom Nicklin of the National Western Gas Board(NWGB) or British Gas Corporation.

Stretford Operation

- An example of a process using O_2 to oxidize H_2S is the stretford process, which is licensed by the British Gas Corporation.
- In this process the gas stream is washed with treating solution(an aqueous solution of sodium carbonate, sodium vanadate and anthraquinone disulfonic acid).
- Sodium carbonate can remove all carbon dioxide, when it exists in small percentages.

Stretford Operation

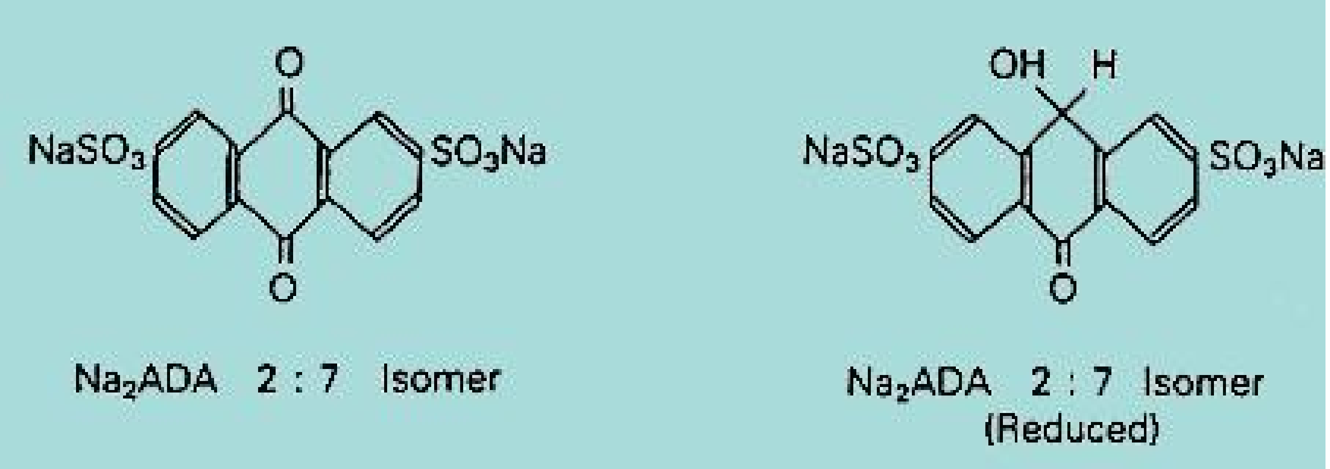
- Removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process.
- Stretford process employs a solution containing vanadium salts and anthraquinone disulfonic acid.
- Most hydrogen sulfide removal processes return the hydrogen sulfide unchanged, but if the quantity involved does not justify installation of a sulfur recovery plant (usually a Claus plant) it is necessary to select a process that directly produces elemental sulfur.

Stretford Operation

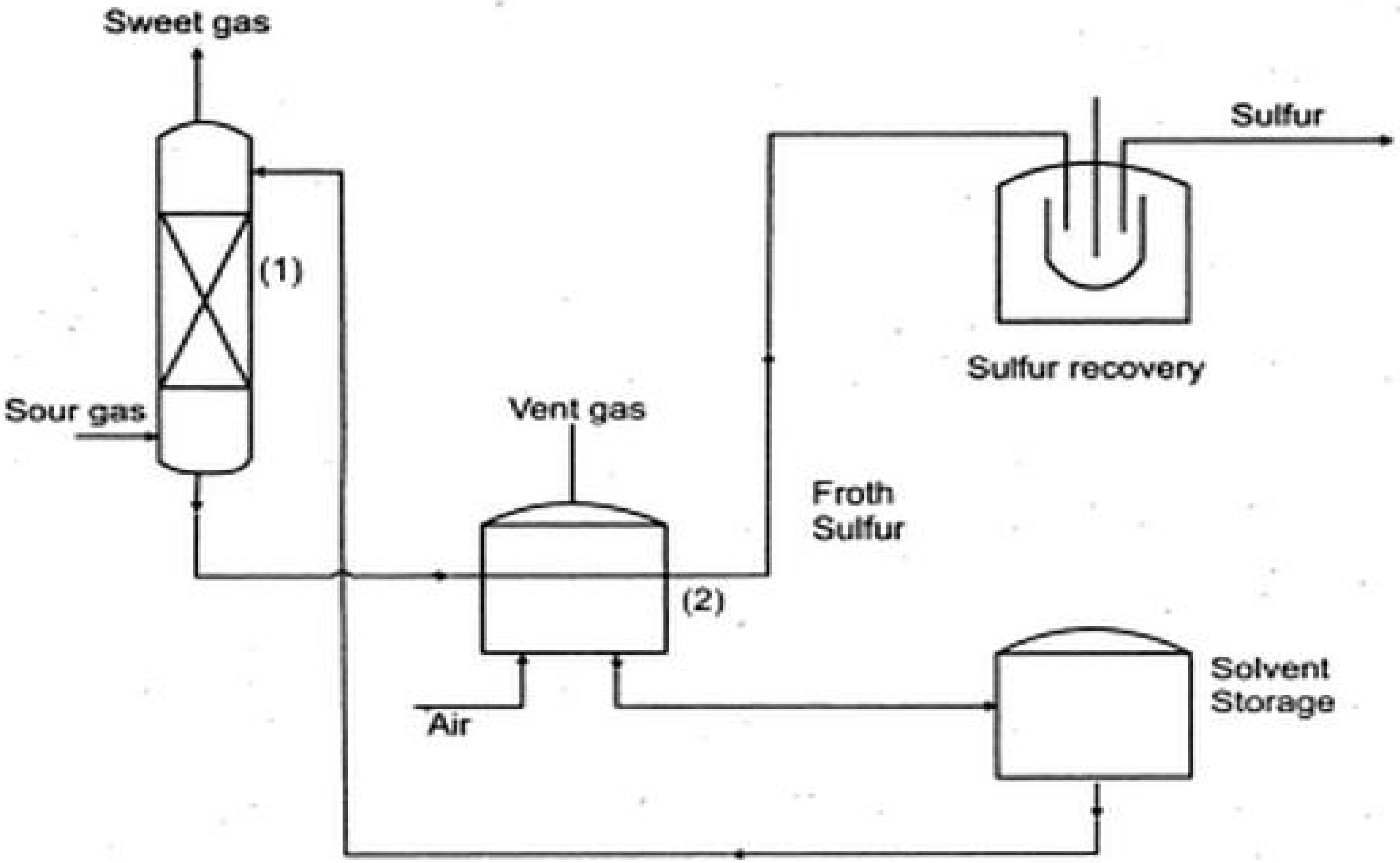
- Absorption and regeneration are based on the "Redox reaction" that causes the catalyst effects of anthraquinone disulfonic acid (in short, ADA)and vanadate in a weakly alkaline solution.

Chemistry

- $2H_2S + 2Na_2CO_3$ -> $2NaHS + 2NaHCO_3$
- $2NaHS + 4NaVO_3 + 4NaHCO_3$ -> $2S + Na_2V_4O_2 + 4Na_2CO_3 + 3H_2O$
- $Na_2V_4O_2 + 2Na_2ADA + 2Na_2CO_3 + 3H_2O$ -> $4NaVO_3 + 2Na_2ADA(Redured) + 2NaHCO_3$
- $2Na_2ADA(Reduced) + O_2$ -> $2Na_2ADA + 2H_2O$



Stretford Process



Process description

- Gas to be treated flows counter-current to the absorbing solution in the absorber and H_2S is removed by the reaction with the absorbing solution.
- Packings used in the absorber are usually splash-type plates designed in a specific manner.
- Absorbing solution is delayed at the bottom of the absorber and hydrogen sulfide in the solution is converted to elemental sulfur as a result of the reaction.

Process description(Contd…)

- Then solution is sent to the oxidizer, where a supply of air is received to regenerate the solution completely and to float elemental sulfur in the slurry.
- Froth of the sulfur slurry is concentrated by a filter or a centrifuge to form sulfur cake, which is reslurried with water and heated to recover molten sulfur of high purity from the sulfur separator.
- On the other hand, the solution regenerated in the oxidizer is sent to the solvent storage and then pumped up to the absorber.

Gasoline treatment

- Offending compound in gasoline are doctored by contacting with different chemicals.
- Sulfur content of gasoline causes serious problems because Low molecular weight mercaptans are volatile, highly toxic, corrosive, and have an objectionable odour.
- High toxicity and volatility of these mercaptans cause serious environmental problems during storage and transportation of such hydrocarbon raw materials.
- Presence of hydrogen sulfide (H_2S) and mercaptans reduce octane number and also cause corrosion with furnishing of bad smell.

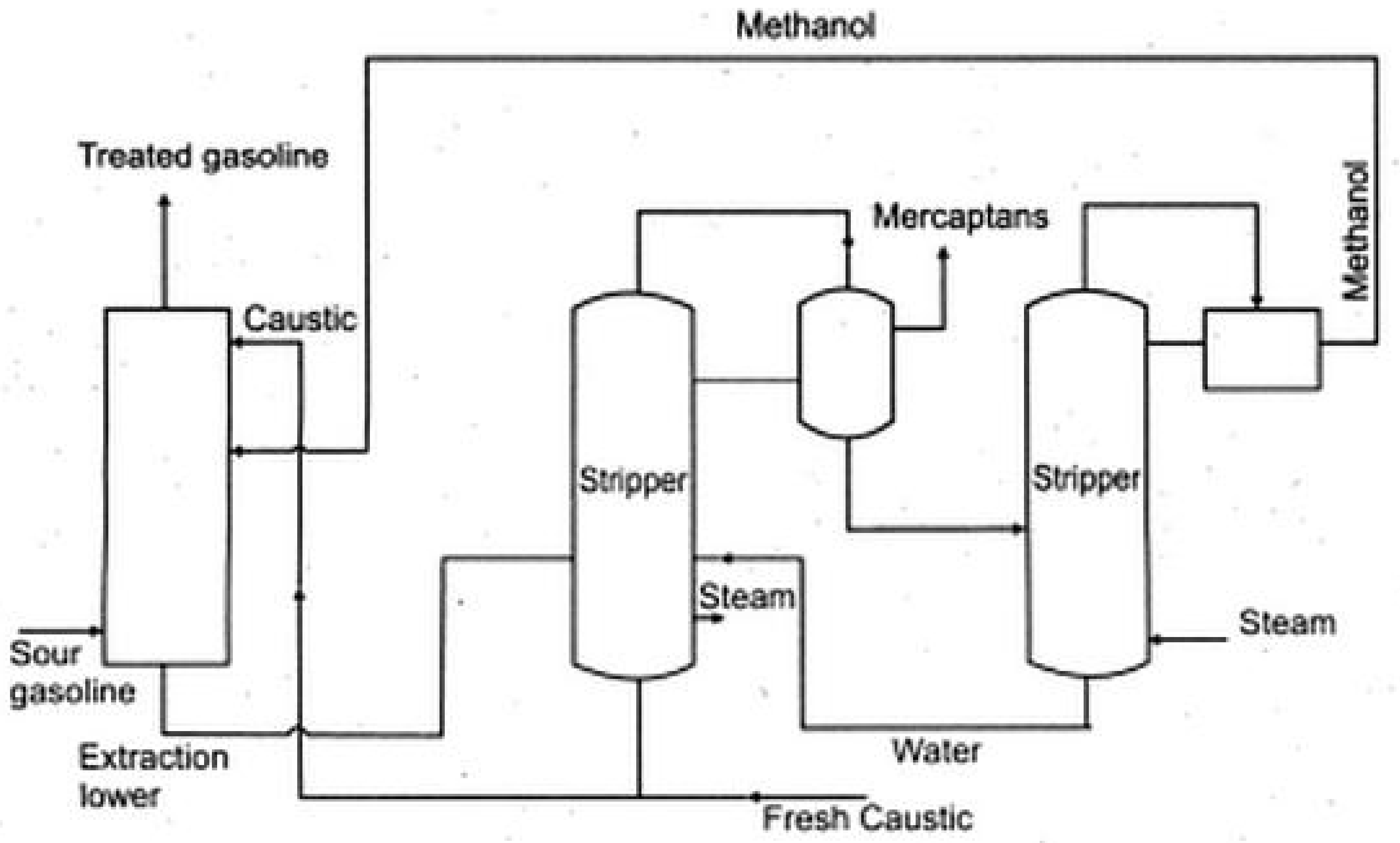
Gasoline treatment

- Copper Chloride Process
- Inhibitor Sweetening
- Caustic & Methanol(Unisol Process)
- Dualayer Process
- Lead Doctoring of Gasoline
- Merox Sweetening
- Sulfuric Acid Treatment
- Catalytic Desulfurization

Unisol process

- Unisol or caustic methanol process uses methanol at the center of the packed treating column and caustic soda throughout the entire length of the column.
- Sour gasoline is passed through this column to extract H_2S and mercaptans.
- Small amounts of methanol are lost with the gasoline.
- Methanol must be distilled after. it (and mercaptans) has been steam stripped from the caustic.

Unisol process



Unisol process

- Unisol process is a regenerative method for extracting not only mercaptans but also certain nitrogen compounds from sour gasoline or distillates.
- Gasoline, free of hydrogen sulfide, is washed counter currently with aqueous caustic-methanol solution at about 40^0C (100^0F).
- Spent caustic is regenerated in a stripping tower (145^0C to 150^0C, 290^0F to 300^0F), where methanol, water, and mercaptans are removed.

Dualayer processs

- Highly concentrated potassium cresylate solution is employed as solvent.
- Higher boiling mercaptans are less readily extracted than the lower boiling mercaptans, treatment of these stocks is easy.
- Similar to Unisol process, here the contact between dualayer agent & sour gasoline is brought out in at least two stages at slightly higher temperature than Unisol process(i.e. 40^0C to 50^0C).

Dualayer processs

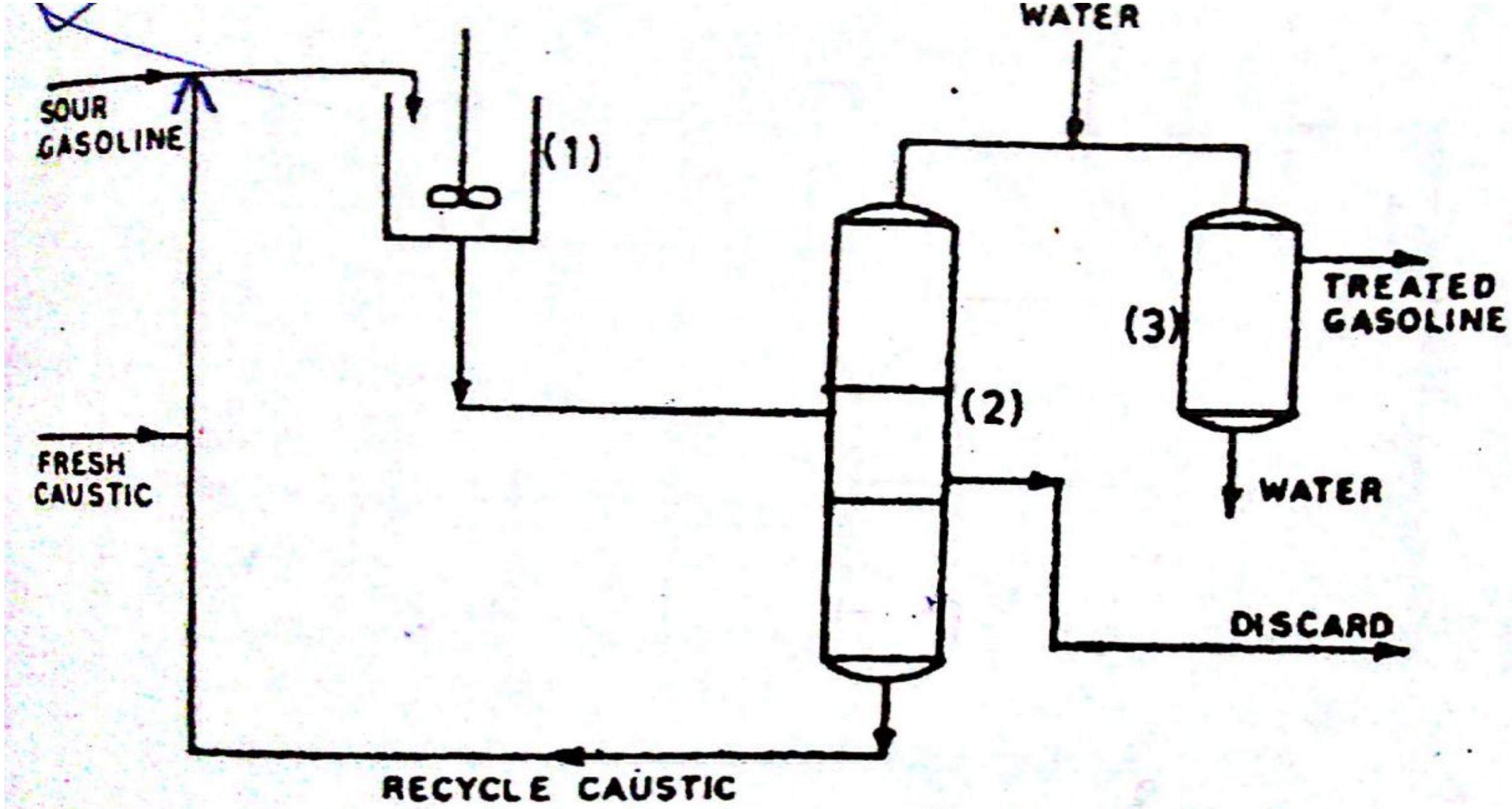


Fig. 4.5*b* Dualayer Process

(1) Mixer
(2) Column Settler
(3) Water Washer and Settler ... ...

Lead doctoring of gasoline

- Mercaptans present in the gasoline are converted into disulphide by treatment with doctor's solution and sulphur.
- $2RSH + Na_2PbO_2 \rightarrow Pb(RS)_2 + 2NaOH$
- $Pb(RS)_2 + S \rightarrow PbS + RSSR$
- $PbS + 2O_2 \rightarrow PbSO_4$
- $PbSO_4 + 4\ NaOH \rightarrow Na_2PbO2 + Na_2SO_4 + 2H_2O$

Lead doctoring of gasoline

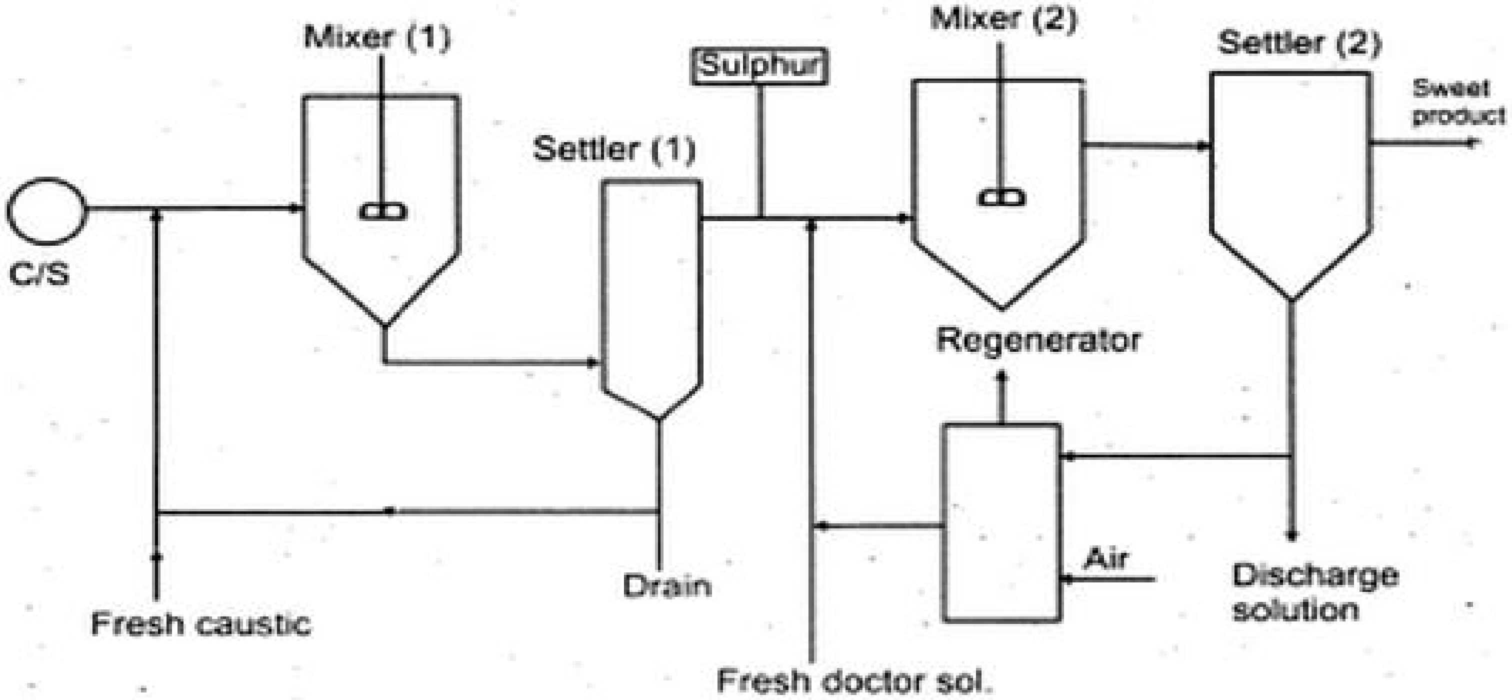


Fig. 4.6 : Lead Doctoring of Gasoline.

Operating Data.

Ratio of Doctor sol. to gasoline 1 : 5

Time of contact 1/2 min. to 1 minute

Sulfur addition and Stirring 5 to 15 min.

Air regeneration temp. 100°C

Pressure 1 to 5 kg/cm^2

Merox(Mercaptan Oxidation)

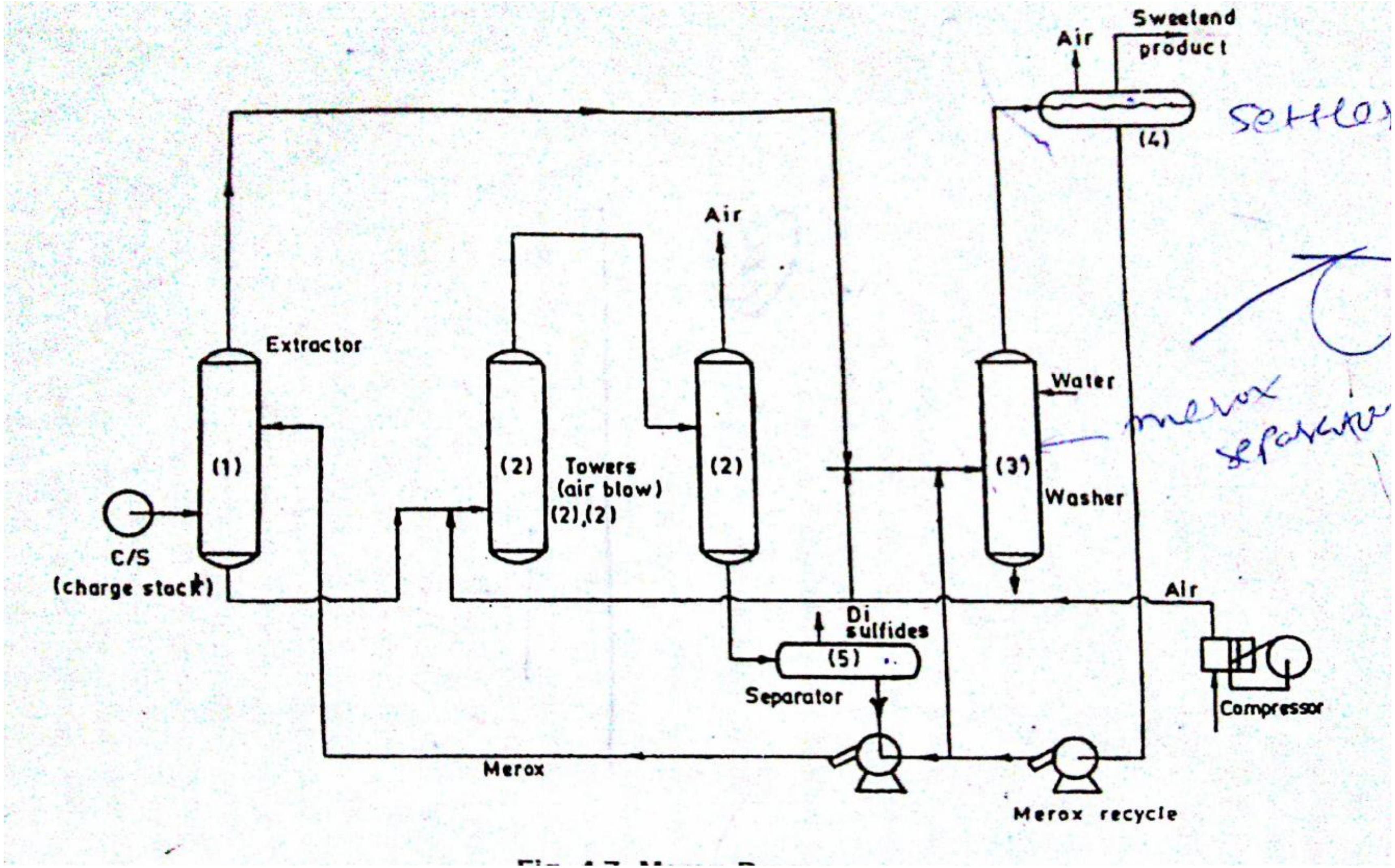
Oxidising mercaptans to disulfides

- Merox process, Developed by UOP (Universal Oil Products), is combination of mercaptan extraction and sweetening techniques involving conversion of active mercaptans to inactive disulfide..
- Sulfur exists in gasoline in different forms such as pure sulfur, hydrogen sulphide (H2S), carbonyl sulphide (COS), carbon disulphide (CS2), mercaptans (RSH) and thiofens.
- Disulfides in gasoline are found to be harmless compared to sulfides.

Reactions

- $RSH + NaOH \Leftrightarrow RSNa + H_2O$
- $2\ RSNa + \frac{1}{2}\ O_2 + H_2O \Rightarrow RSSR + 2\ NaOH$
- $2\ RSH + \frac{1}{2}\ O_2 \Rightarrow RSSR + H_2O$

Merox sweetening



Merox sweetening

- This process is base on removal of low molecular weight mercaptans (methyl to propyl mercaptans) by extraction with aqueous sodium hydroxide and subsequent oxidation of high molecular weight mercaptans to alkyl disulphides.
- This process reduces the total sulfur content up to 30% and mercaptan content is reduced to 5 ppm.

Catalytic Desulfurization

- Hydrotreating (or hydrodesulfurization) is an extremely versatile process that can be applied to straight-run products, cracked products, feedstocks to catalytic reforming and catalytic cracking, and lubricating oils.
- It has two purposes
  - treatment of petroleum fractions to remove such impurities as sulfur, nitrogen, and metal compounds, thus preventing corrosion and catalyst poisoning
  - treatment of products to improve color and odor.
- Hydrotreating is the most common process for pretreating catalyst reformer and catalyst cracker feedstocks to remove sulfur and nitrogen, which can poison the catalyst.
- This pretreatment prolongs catalyst life and the time between regeneration cycles in the reformer and the cracker.

Importance of Hydrodesulfurization

- Prevention of poisoning of the metal catalysts by sulfur.
- Control of pollution by SO_2 produced in the combustion of gasoline.
- Removal of the unpleasant odour caused by the presence of sulfur.

- **Hydrotreating**: A process used in the oil industry to remove objectionable elements such as nitrogen, sulfur, oxygen and metals from petroleum distillates by reacting them with H_2 over a catalyst.

- **Hydrodenitrogenation (HDN):** is the removal of nitrogen from nitrogen containing feeds in the form of NH_3. The resulting products are hydrogenated .

- **Hydrodesulfurisation (HDS):** is the removal of sulfur from sulfur containing feeds in the form of H_2S. The resulting products are hydrogenated .

- **Hydrodeoxygenation (HDO) and hydrodemetalization** are the removal of oxygen and metals from the feed.

Catalytic Desulfurization

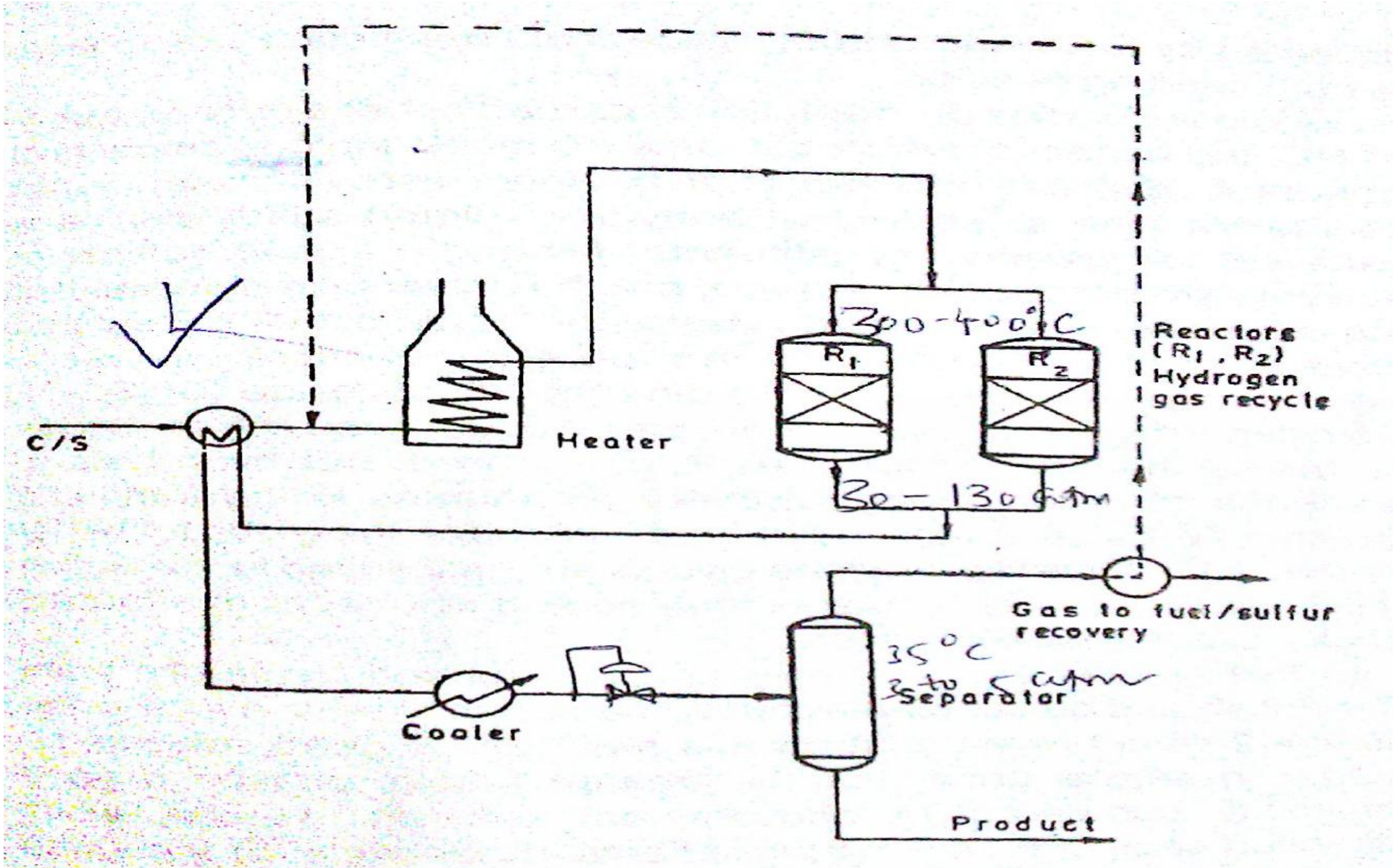


Fig. 4.9 Catalytic Desulfurisation.

Catalytic Desulfurization

- Process convert S to H_2S by reaction with hydrogen in the presence of catalyst.
- Gas oil feed is mixed with makeup and recycled hydrogen, and is heated before flowing into the fixed- bed reactor containing catalyst.
- Temperature of feed entering the reactor is regulated between 290° and 425°C (550° and 800°F).
- Coking reactions become much more prevalent, however, when operating temperatures approach 415°C (780°F), Coke is deposited on the catalyst, reducing catalyst activity and necessitating regeneration, which results in emissions.
- Sulfur and nitrogen compounds are converted in this reactor to hydrogen sulfide (H_2S) and ammonia.
- Reaction product is cooled and sent to a high-pressure separator (flash drum), where the hydrogen-rich stream is flashed from the reactor product and recycled.

Copper chloride sweetening process

- $4CuCl_2 + 4RSH \rightarrow 2RSSR + 4HCl + 4CuCl$
- $4CuCl + 4HCl + O_2 \rightarrow 4CuCl_2 + 2H_2O$

Copper Chloride Process

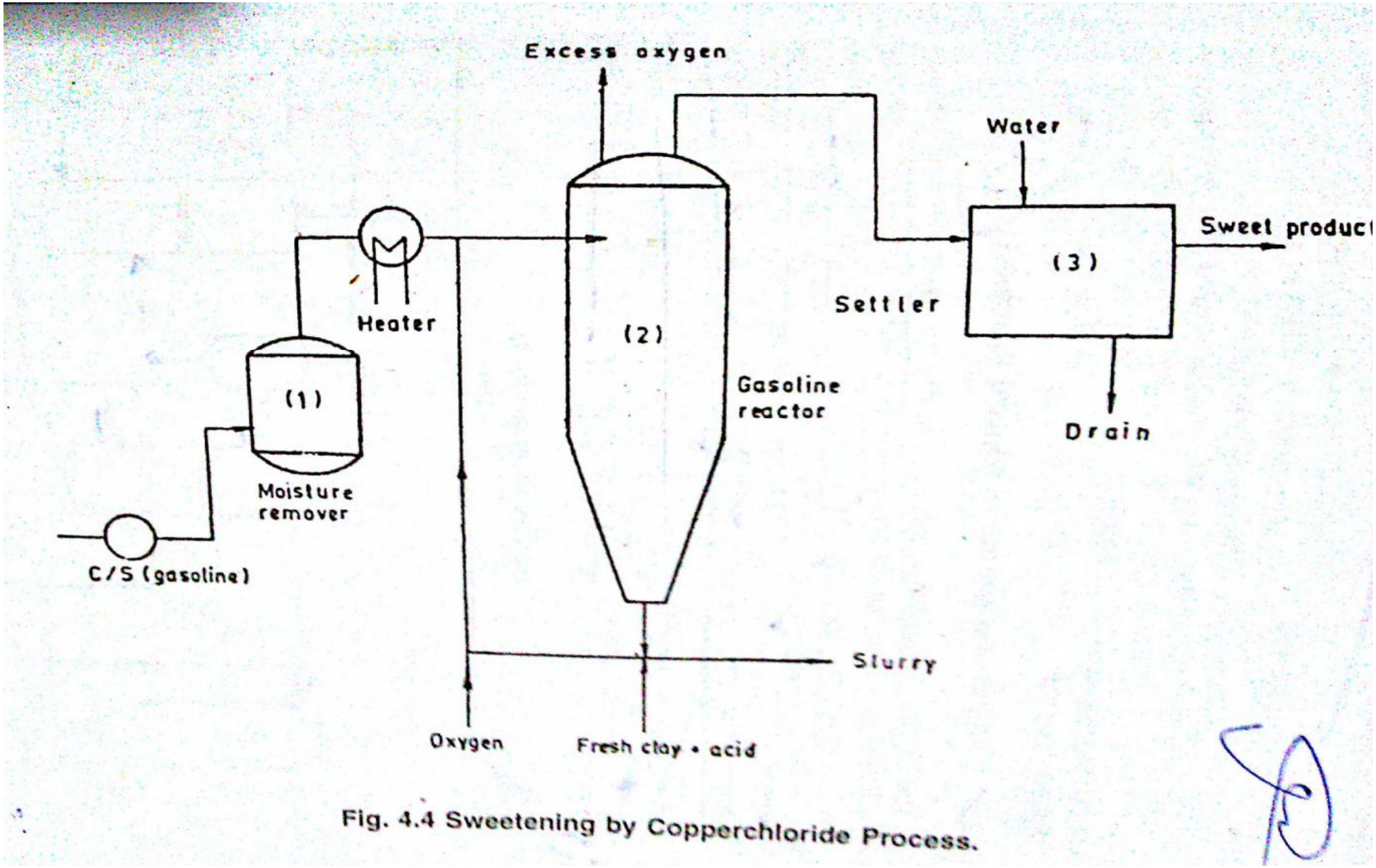
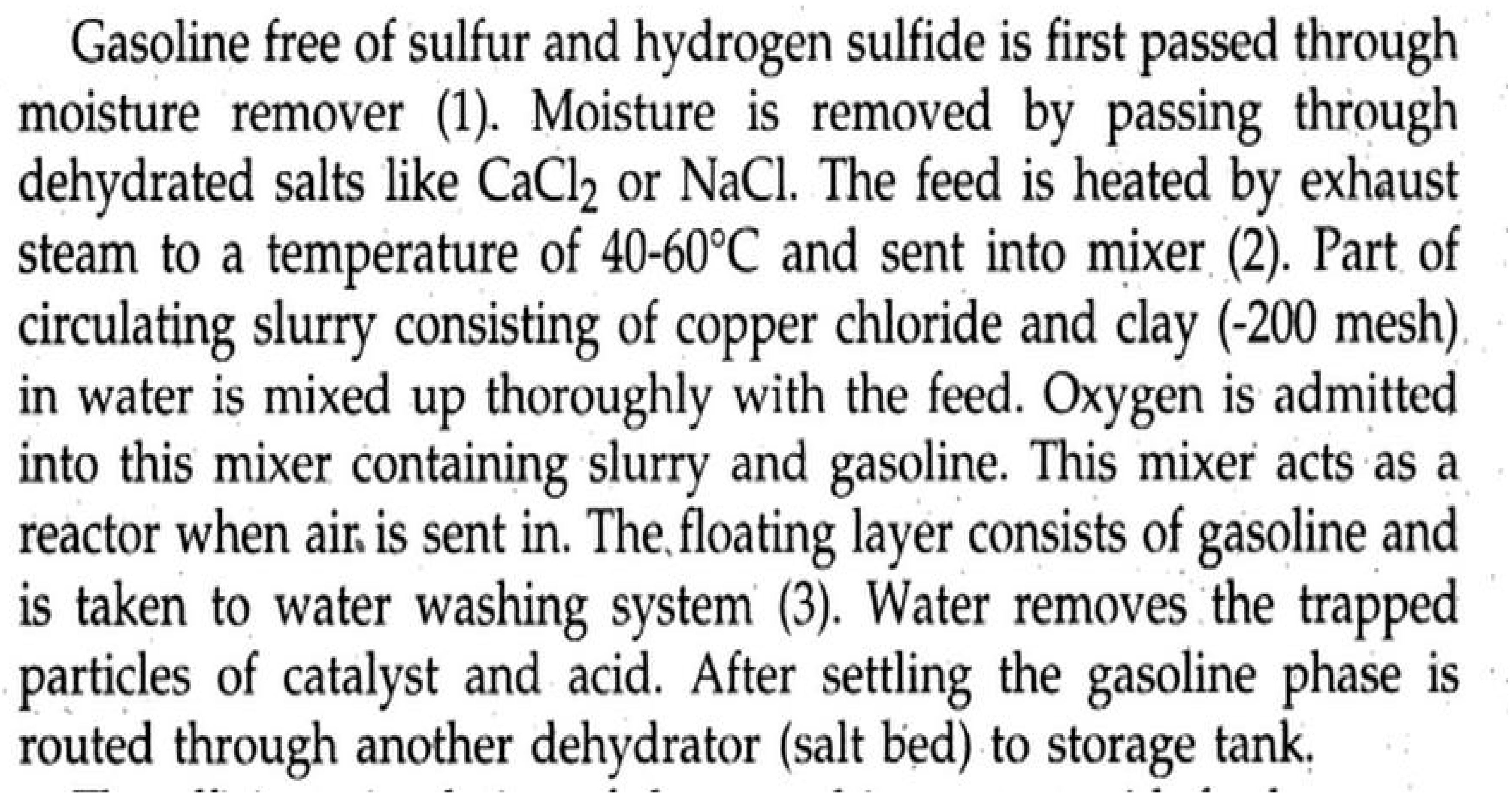


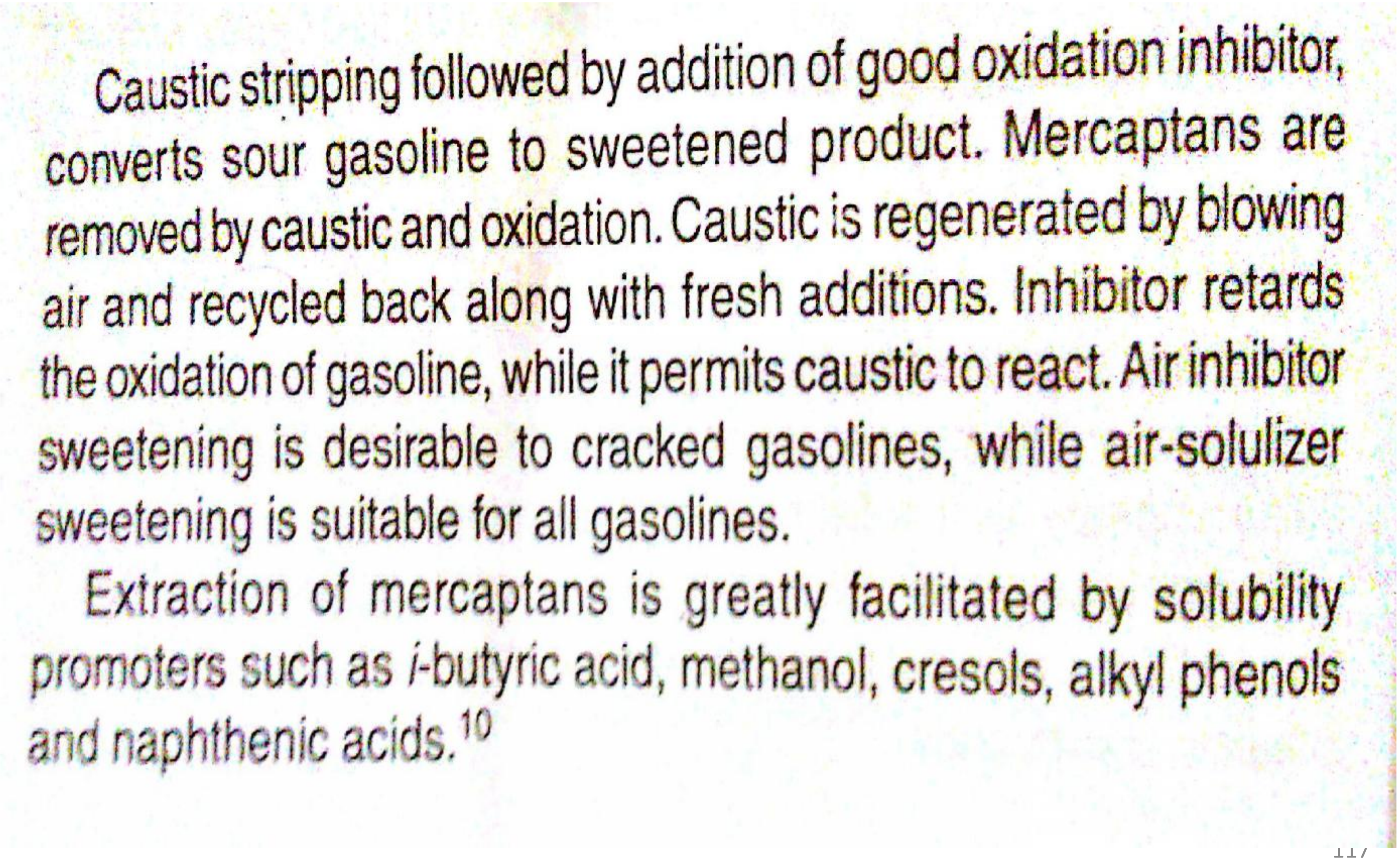
Fig. 4.4 Sweetening by Copperchloride Process.

Copper Chloride Process



Gasoline free of sulfur and hydrogen sulfide is first passed through moisture remover (1). Moisture is removed by passing through dehydrated salts like $CaCl_2$ or NaCl. The feed is heated by exhaust steam to a temperature of 40-60°C and sent into mixer (2). Part of circulating slurry consisting of copper chloride and clay (-200 mesh) in water is mixed up thoroughly with the feed. Oxygen is admitted into this mixer containing slurry and gasoline. This mixer acts as a reactor when air is sent in. The floating layer consists of gasoline and is taken to water washing system (3). Water removes the trapped particles of catalyst and acid. After settling the gasoline phase is routed through another dehydrator (salt bed) to storage tank.

Inhibitor Sweetening



Caustic stripping followed by addition of good oxidation inhibitor, converts sour gasoline to sweetened product. Mercaptans are removed by caustic and oxidation. Caustic is regenerated by blowing air and recycled back along with fresh additions. Inhibitor retards the oxidation of gasoline, while it permits caustic to react. Air inhibitor sweetening is desirable to cracked gasolines, while air-solulizer sweetening is suitable for all gasolines.

Extraction of mercaptans is greatly facilitated by solubility promoters such as *i*-butyric acid, methanol, cresols, alkyl phenols and naphthenic acids.[10]

Thank you