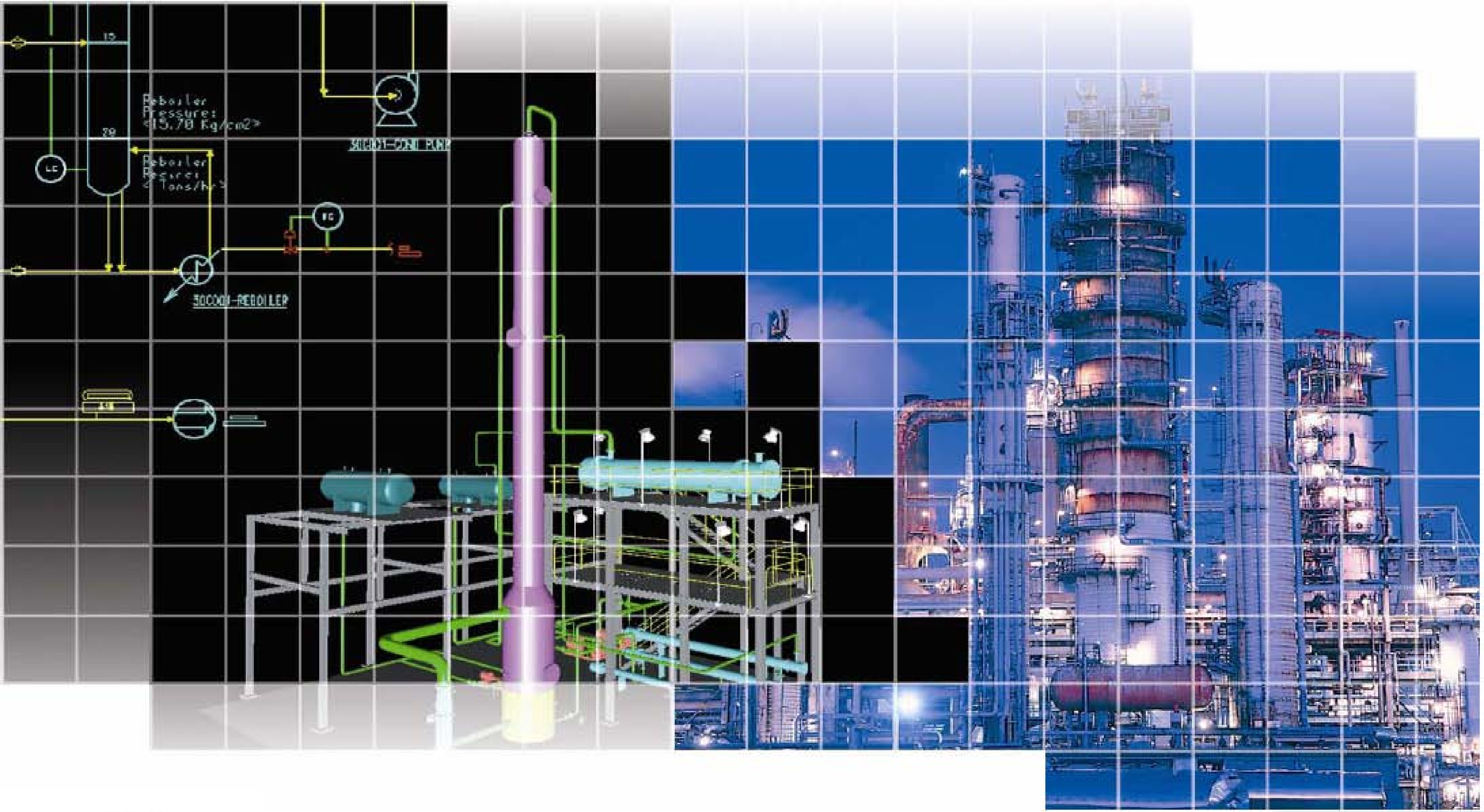


Lect./9

Finishing Processes

☐**Primary processes** is to produce the required amounts of the various products from the available crude.

The 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.

❑ ***Secondary refining processes*** **(finishing or treating processes), are required to give the products acceptable with respect to the above criteria.**

Main Finishing Processes

- **The removal of the objectionable gases (Acid gas removal).**
- **The removal of the objectionable odors.**
- **The improvement in storage stability.**
- **The improvement in performance characteristics.**
- **The removal of water and particulate matter.**

A) The removal of the objectionable gases

1) Hydrogen sulphide (H_2S)

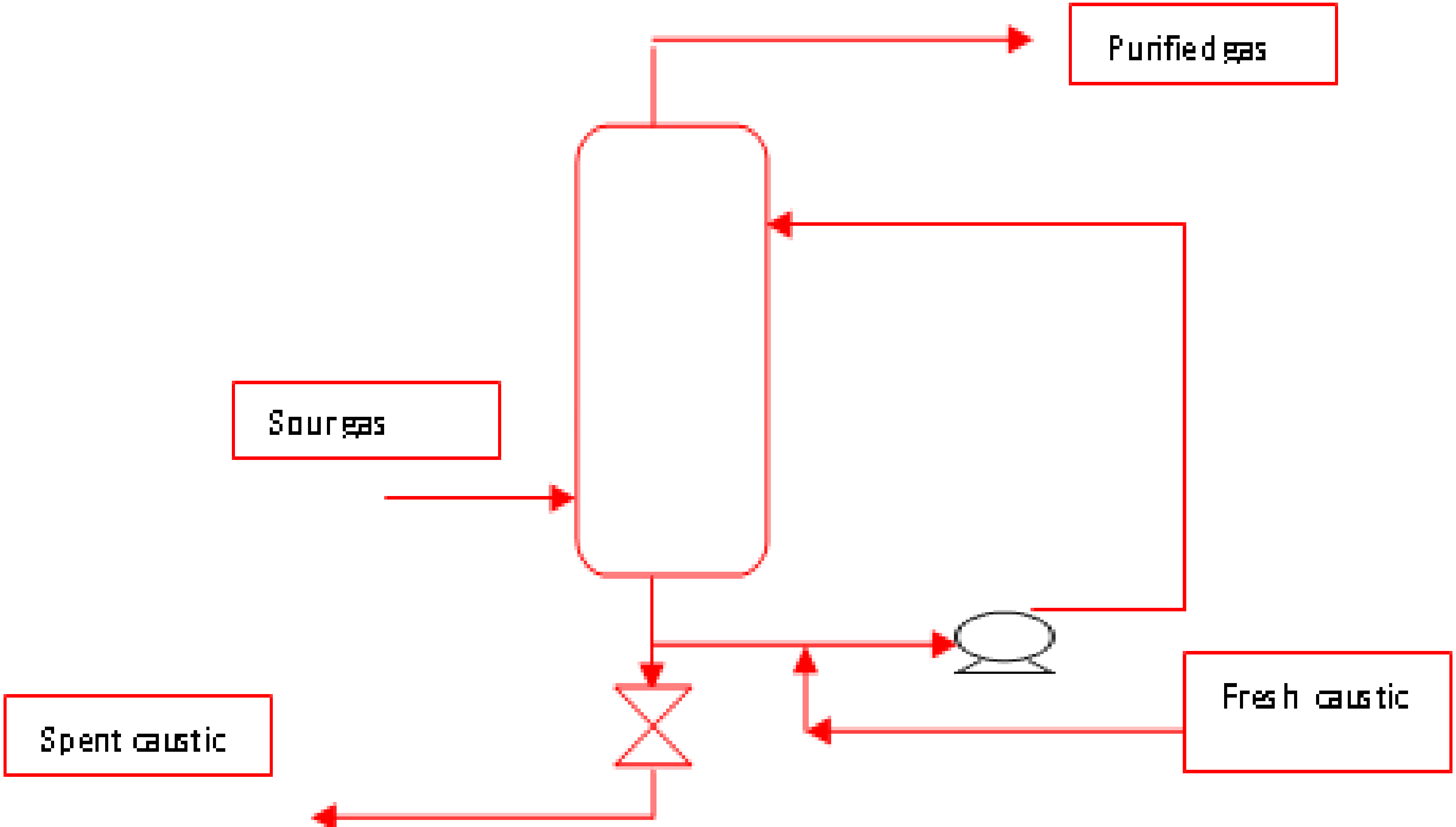
Removed from products because :

- ✓Toxic
- ✓Foul smelling
- ✓Corrosive, and
- ✓Traces of it may seriously contaminate regenerative treating solvents such as a solutizer used for final sweetening of the products.

A) Scrubbing with caustic soda

- **Widely used process for the removal of H_2S , mainly because it simultaneously removes other constituents such as CO_2 , carbonyl sulphide, lower aliphatic mercaptans, phenols fatty acids and naphthenic acids.**
- **The disadvantage of this processes is that there is no known cheap method of regenerating the spent soda,**
- **If H_2S is present in gross amounts, as is frequently in crude gases, especially the C_2 -C_3 fractions , a regenerative method of extraction such as the girbotol method is more generally used.**
- **This method is more economical than caustic washing but caustic washing may still be required as a final cleaning-up operation for the removal of the last traces of H_2S.**

- The combination of the two processes not only provides a very low H2S content economically but also safe guards against high sulfur contents in the treated products should there be a temporary failure of the regenerative treating plant.
- In the caustic washing of gases rather weak solutions of 2-10%wt NaOH have to be used to prevent the deposition of sodium sulphide crystals.
- The reaction proceeds almost to the complete conversion of NaOH to NaHS.
- Traces of H2S often appear in fractions much heavier than C2 -C3 fraction because of a slight breakdown of sulfur compounds owing to pyrolysis during re-distillation or a similar operation. Caustic soda may be employed for its removal.



Purified gas

Sour gas

Fresh caustic

Spent caustic

Fig ( ) H_2S removal from gases by caustic washing

B) Girbotol process

- **Hydrogen sulphide and carbon dioxide readily combine with aqueous solutions of certain alkanol amines at temperatures usually close to ambient ,**
- **and may be driven off from the fat solutions by heating to about 100 ^{o}C .**
- **The reaction with hydrogen sulphide is :**

- $2\ RNH_2 + H_2S \rightleftharpoons (RNH_3)_2S$
- Amine (mono- di and tri ethanol amines and methyl di ethanol amine)

- The conventional equipment , comprising a bubble- cup tower together with a bubble cup tower for regeneration.
- The treating temperature is 5 to 10 ^{o}C above the dew point of the gas to ensure that no hydrocarbons liquid condenses out of the plant.
- The girbotal process is the most widely used method for the regenerative removal of H_2S from both gases and liquids.
- Its use is not only in refineries but also for oilfield treatment of natural gases and LPG.
- The choice of the proper amine and solution depends on the composition of the gas to be treated and the final purity desired.

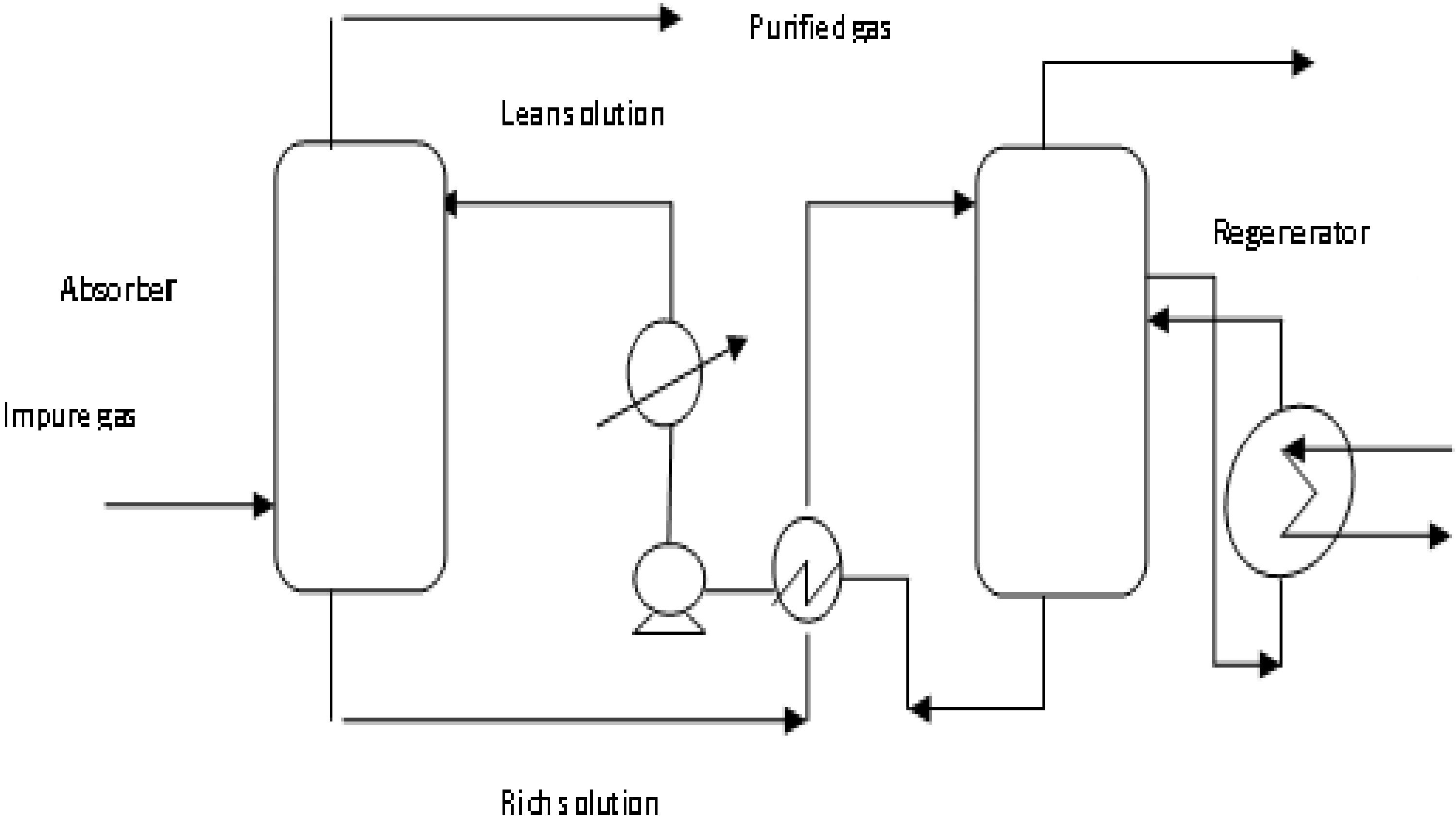


Fig ( ) Girbotol process

2)Carbon dioxide (CO2)

- Carbon dioxide is frequently found in natural gas, and is also present in the products of catalytic crackers since regenerated catalyst always carries with it a small quantity of carbon dioxide.
- Its removal is rarely a direct aim but the major part of it will be removed by a caustic wash applied for the removal of H2S.
- When CO_2 removal is a direct aim one of the regeneration processes such as Girbotol process would normally be used.

B) The removal of the objectionable odors

(Sweetening Process)

- The object of sweetening processes is to ensure that the finished products do not have objectionable odors.
- The objectionable odors are normally attributed to traces of mercaptans.
- it is necessary either to remove them by

1)extractive processes or

2) by hydrodesulphurization ,

3) or to covert them into innocuous disulphides.

1)Copper Chloride Process

- The copper chloride process is used to sweeten gasolines and kerosenes by the direct oxidation of mercaptans to disulphides, using cupric chloride as the oxidizing agent.
- The basic reactions of the process may be expressed as follows :

Sweetening :

$$CuCl_2 + 2RSH \rightarrow CU(SR)_2 + 2HCl$$

Cupric chloride   Mercaptan   Cupric mercaptide   Hydrochloric acid

$$Cu(SR)2 + CuCl2 \rightarrow Cu2Cl2 + R\text{-}S\text{-}SR$$

Cupric chloride   Disulphide

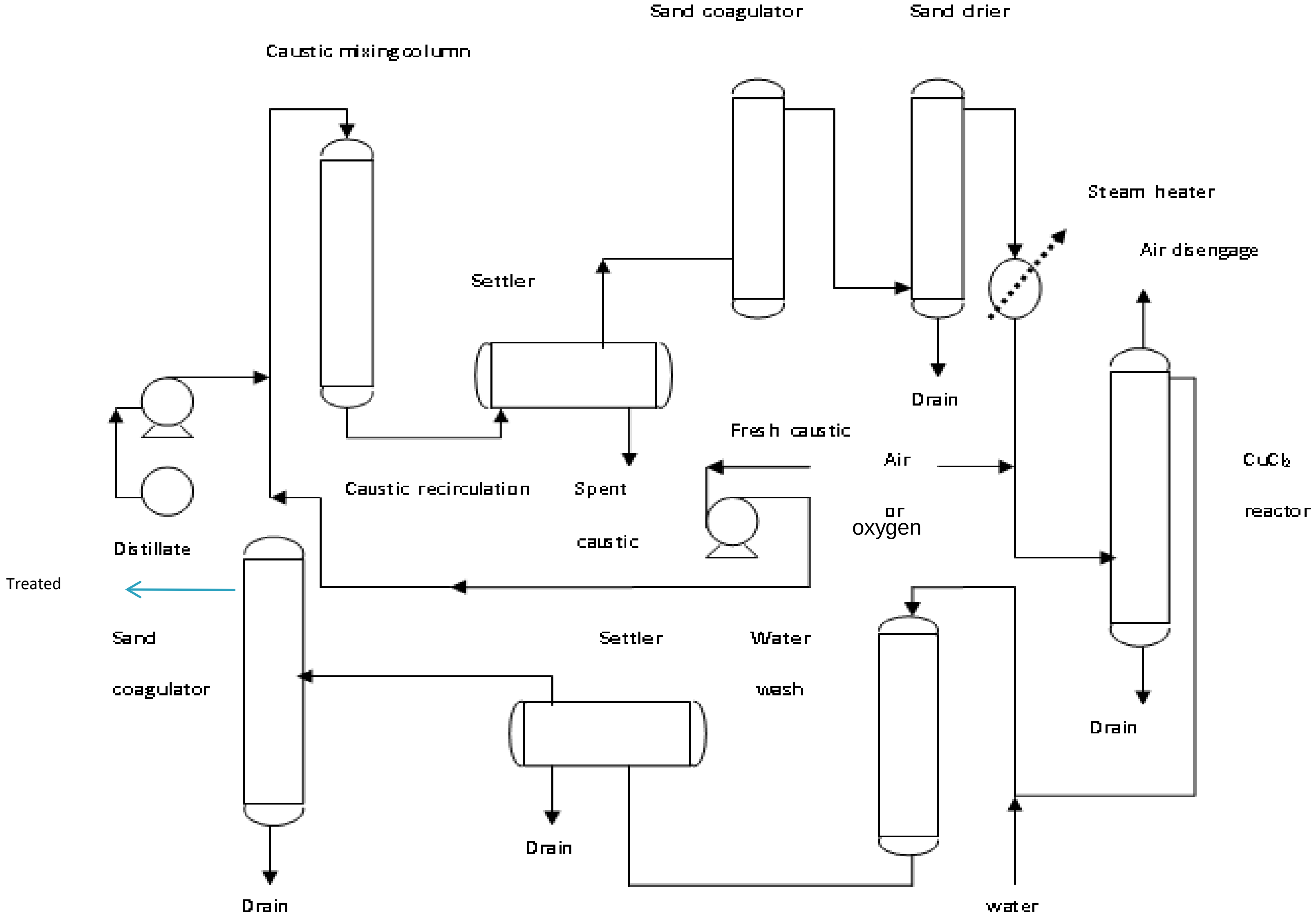
Regeneration

$$Cu2Cl2 + 2HCl \rightarrow Cu2Cl2\ 2HCl$$

Chlorocuprous acid

$$Cu2Cl2\ 2HCl + \tfrac{1}{2}\ O2 \rightarrow 2CuCl2 + H2O$$

Treated



Copper Chloride Sweetening

Process Description

- 1)The sour charge is caustic washed to remove traces of hydrogen sulphide which would otherwise deactivate the cupric chloride.
- 2) It then pass :
- A) firstly through a sand coagulator to remove any caustic and / or water haze
- B) secondly through a rock salt drying lower to ensure complete removal of free water, which would adversely affect the water balance in the reactor.
- 3)After passing through a pre-heater to raise the temperature sufficiently to dissolve the water formed during the process, air or oxygen is injected into the line, and the dried and oxygenated feed flows upwards through the reactor which contains a bed of fullers earth impregnated with cupric chloride.
- 4)The sweetened product is water washed to remove traces of acidity, clarified from water haze in an up-flow sand coagulator and passed to storage.

2) Merox Process :

- ➢Developed by UOP (Universal Oil Products),
- ➢ is combination of mercaptan extraction and sweetening.
- ➢The combined process is applicable to all gasoline and lighter boiling range fractions;
- ➢ the sweetening process is applicable to many jet fuel and kerosenes.

a)Merox Extraction:

✓Removal of mercaptans by extraction starts with dissolving them in caustic soda based on the following reaction:

$$RSH + NaOH \rightleftharpoons NaSR + H_2O$$

✓ Since the reaction is reversible it is impossible to get complete removal of mercaptans by extraction without the use of an excessive amount of caustic soda solution.

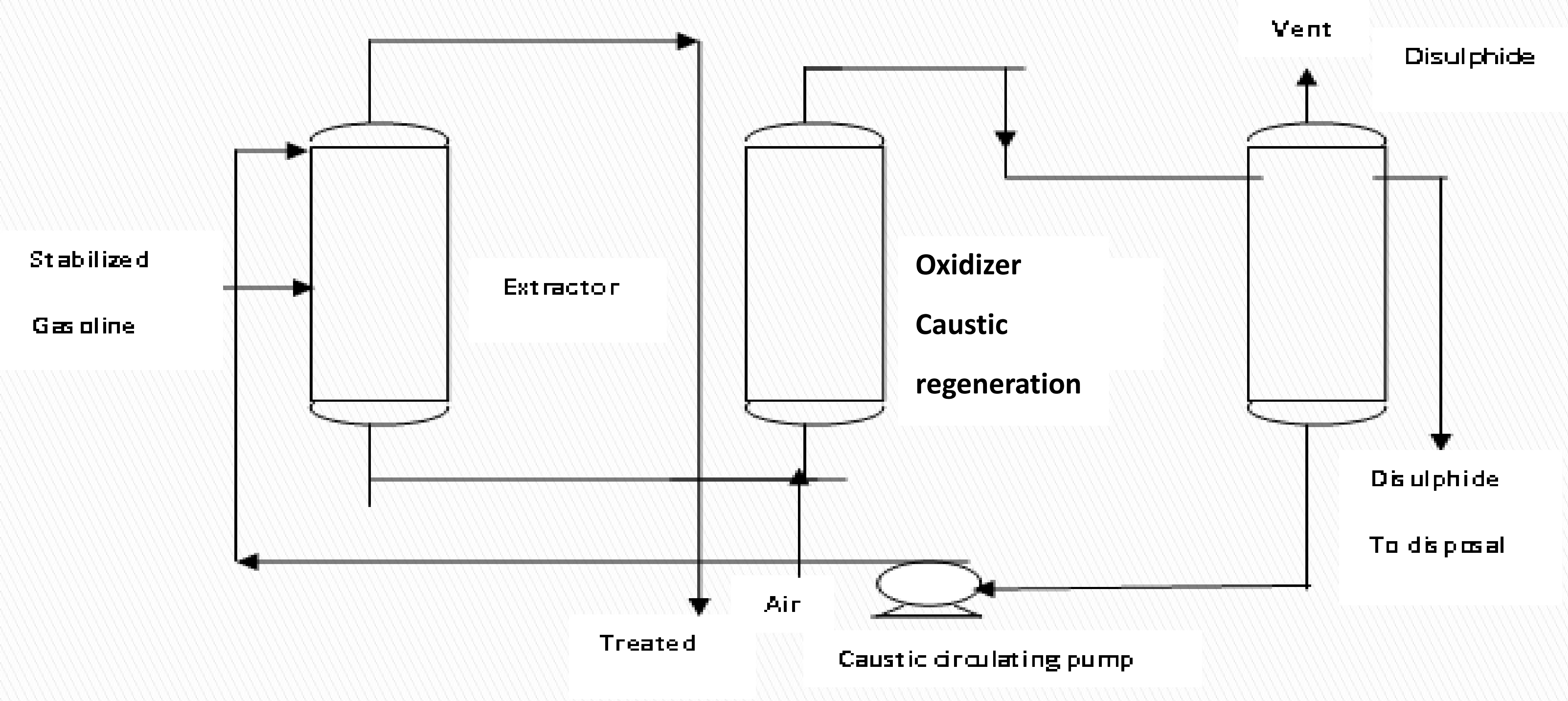
The forward reaction is favored by

- ❑low temperature,
- ❑ low molecular weight of mercaptan and
- ❑high caustic concentration.
- ❑It is also promoted by the use of compounds that increase the solubility of the mercaptan in the aqueous phase, of these methanol, isobutyric acid and cresols.

2- The caustic is generated ,after separation from hydrocarbons by blowing with air in the presence of a catalyst at ambient temperature the reaction proceeding according to the reaction :

$$2NaSR + 1/2\ O_2 + H_2O \rightleftharpoons RSSR + 2\ NaOH$$

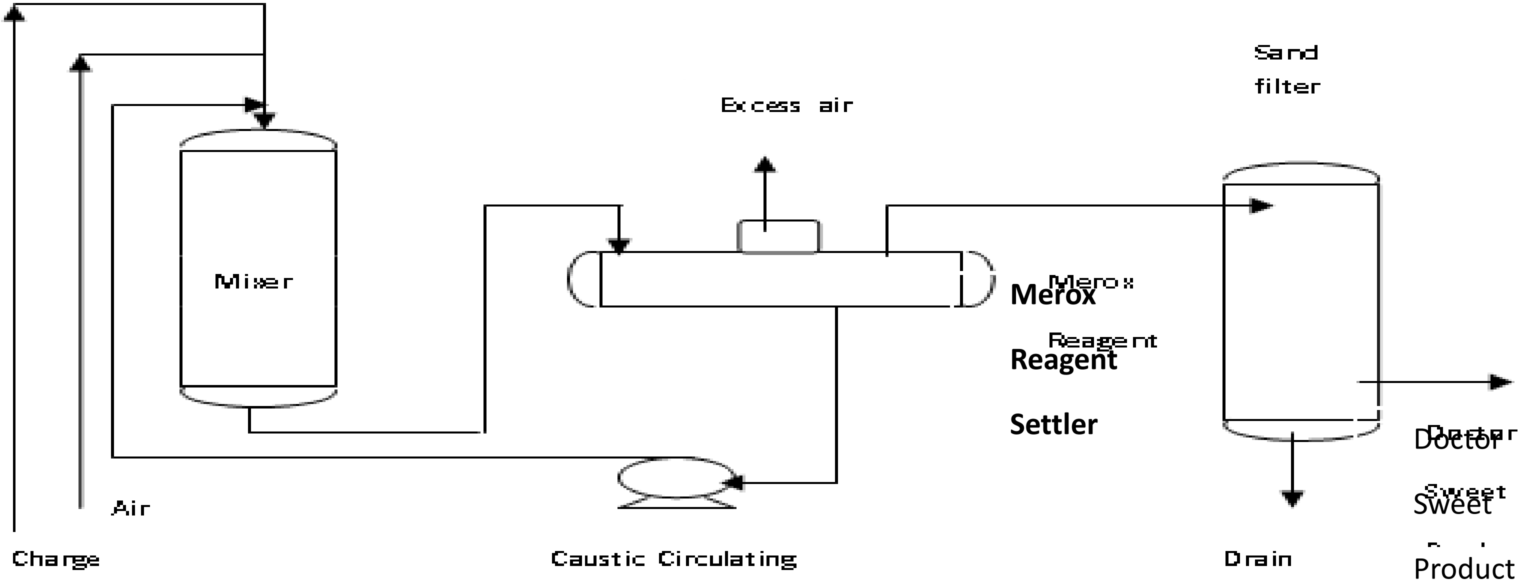
- The **disulphide** so formed are **insoluble in caustic soda** and are removed in a gravity separator, the caustic is being re-circulated for further use.
- The catalyst which consists of an **iron group metal chelate** , may be in solution in the caustic, in which case the caustic and air are brought into contact in a reactor such as an orifice column, a mechanically stirred reactor or some other type of gas/liquid contactor.
- Alternatively the catalyst may be supported on a carrier, in which case the caustic and air are passed together over a packed bed.



Merox Extraction

b)Merox Sweetening:

- Sweetening is achieved by blowing a caustic hydrocarbon mixture with air in the presence of the catalyst where by disulphide are formed according to equation (2), and dissolve in the material being treated .
- As in the above mentioned regeneration process, the catalyst may be in solution in the caustic or held on carrier, and the process is carried out as described.



Merox Reagent

Settler

Doctor

Sweet

Product

(0.0004% RSH)

Merox Sweetening

c) Combined Operation:

The combined extraction/ Sweetening operation is carried out by a combination of the extraction and sweetening processes.

C) The removal of water and particulates matter.

Why water and matter particulates must be removed from refinery products

1)Water and particulate matter in the fuel can have disastrous effects on gas turbine blades.

2) Free water may cause corrosion through out a fuel distribution system.

3) Particulate matter may block filters or the fine orifices of fuel injection and burner.

Water may be removed by :

1)Physically
2) Chemically
3) Electro- statically

Particulate matter may be removed by:

1) Water washing
2) Filtration

Processes:

1)Salt Dryers:

- Used to remove water **from** water primary distillation products and to control the water content both before and after secondary processing
- The product is passed through a vertical drum filled with suitably graded rock salt.
- Rock salts are not powerful desiccants; it will remove the free water but not dissolved water.
- If more dissolved water has to be removed it is usual to use calcium chloride in the dryer.

2)Electrostatic Coalescers :

- Uses electrical coalescing for the removal of free water and sodium chloride or calcium chloride for the removal of any residual traces of water.
- The process is used for the dehydration of heating oil, kerosene, jet fuel, diesel fuel and solvents.
- The dehydration product contains no free water but may contain some dissolved water.

3) Sand Coagulators and Filters :

- Vertical drums filled with fine sand are used for removal of particulate matter and water,
- This process have the advantage over salt dryers is not involving the use of chemicals.
- Down flow through the bed and up flow through a water separator will remove gross water but not haze.
- For this purpose the oil must pass upward through the bed with a bottom water drain so that it can emerge clear , and bright from the top of the drum,
- 5 micron peculator filter may be needed for turbo jet fuel.

4) Vacuum Flashing :

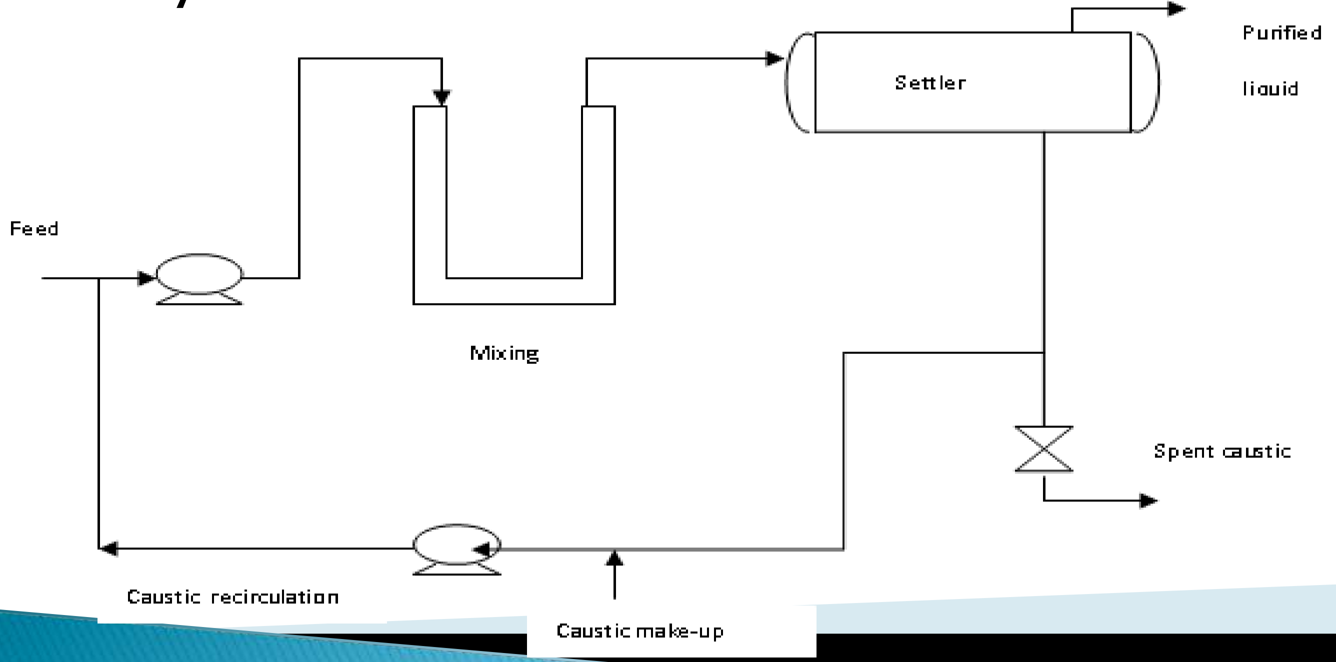
- Where difficulties might be met in the removal of water from high-boiling or viscous products by the previous methods,
- Water may be removed by passing the product through a vessel at a sufficiently reduced pressure to cause the water to evaporates ,
- It is used sometimes for the clarification of lubrication oil.

D) Improvement in Storage Stability

- Owing to their complex composition and the presence of small amounts of N_2, S, organic acids, and oxygen,
- Most petroleum products are subjected to deterioration in storage.
- This storage instability may be noticed by a darkening in color, the formation of gums, and in some cases a significant deterioration in those characteristics that control the performance of the products.
- Instability may be accompanied by a marked degree of corrosiveness due to the presence of organic and/ or inorganic acids

Caustic Extraction

- In addition to the use of caustic soda for the removal of acidic gases and malodorous compounds as described earlier ,
- it is widely used for the removal of substances which cause instability and corrosion.



E) Improvement in Performance

- ✓The performance characteristics of products from primary refining processes are seldom in keeping with the demands of modern machinery and engines.
- ✓It is therefore often necessary to subject the products to secondary refining processes to remove those compounds that have an adverse effect on performance.

Performance improvement processes

1) SO2 Extraction :

- ✓ Liquid SO_2 is very selective solvent for removal of aromatic hydrocarbons .
- ✓ SO_2 treatment removes aromatics and some polar compounds, including sulfur , gum and color constituents , as well as olefins.
- ✓ The process is used in the manufacture of premium kerosene the removal of aromatics leads to better burning properties.

2) H2SO4 Treatment :

- This process is used for the removal of sulfur and thiophene from aromatic streams .
- It is less applicable now a days as other treating methods are available .
- This process may be applicable for the pretreatment of straight run naphtha that are to be reformed.

3) Hydrodesulphurization :

- Hydrodesulphurization is the most modern and effective processes for the removal of sulfur from oil products and for general improvement in the quality of refinery streams, including the pretreatment of catalytic reformer feed.
- The process convert S to H_2S by reaction with hydrogen in the presence of catalyst.
- This process is used mainly for the processing of straight run and cracked medium and heavy distillates, while vapor phase hydro-treating is used for the processing of light distillates it operates at lower pressure.

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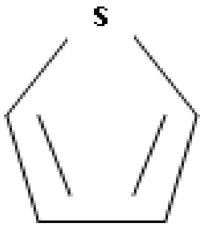
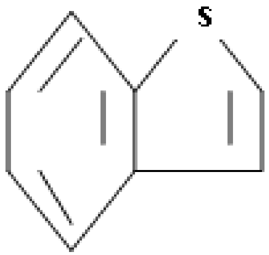
Thiophen:

- Thiophen (XXII) and mono-methyl thiophens have been isolates from gasoline :
- alkyl-thiophens and benzo-hiophens (XXIII) have been isolates from kerosience.
- In gas oil range substituted thiophens, benzo-hiophens and higher polycyclic thiophens are present



(XXII)Thiophen



(XXII) Benzo thiophen

Two general methods of reducing the amount of sulfur have been developed, those which involve

1) solvent extraction of the sulfur compounds and

2) those by which most of the sulfur compounds are decomposed by the use of a catalyst into hydrogen sulfide and the remaining hydrocarbon part of the molecule.

- The solvent extraction processes are not cheap or effective as the catalytic processes in the removal of sulfur because they remove the entire sulfur bearing molecule and at the same time certain hydrocarbons , particularly those with aromatic rings.

- This when the removal of aromatic hydrocarbons as well as sulfur is desirable , the solvent process may be superior.
- H_2SO_4 , HF are an effective solvent, but SO_2 and furfural are more frequently used.
- The solvent process tends to raise the pour point and moderately improve the Diesel Index, but the catalytic processes of desulphurization do not materially affect either of these properties.
- Yields by the catalytic processes may exceed 100% especially if outside hydrogen is used.
- By the addition of H_2 from outside sources more vigorous reaction (decomposition) and hydrogenation can be undertaken, and in the extreme, whole crude oils and residues can be desulphurization.

- By the addition of H_2 from outside sources more vigorous reaction (decomposition) and hydrogenation can be undertaken, and in the extreme, whole crude oils and residues can be desulphurization.
- Desulphurization is a mild selective hydrogenation, so mild that aromatic are not usually hydrogenation to naphthenes. Sulfur is removed as H_2S and the remaining part of the molecule is hydrogenated.
- Mild decomposition result in an evolution of hydrogen which can be recycled for hydrogenation reactions but if higher boiling or refractory stocks are being treated, extra H_2 must be introduced from outside sources to maintain a higher concentration of hydrogen during the reaction.
- Efficiency of desulphurization depends upon the charge stock and severity of treatment, ranging from as low as 50 to 60 % for mild operation to 80 to 99 % and 95 to 98% is not uncommon.

Treating Equipment

The mechanical operations involved in treating are primarily those of

1) *Mixing*
2) *Contacting*
3) *Settling* or *Separating*.

Contacting method :

- The design of mixing columns is normally based on the pressure drop that is available for mixing.
- A total pressure drop of 30 psi is sufficient to give effective mixing.
- Among the type of mixers are *square-angle bends*, *orifice-plate*, *baffle plate columns perforated buckets*, *various mechanical mixers operated by motors*, *jet and nozzle mixer* and *pumps*.

Orifice Column :

- widely used for mixing

$$Q = 17.8 * D^2 * \sqrt{\Delta h}$$

Q= volumetric flow rate Bbl per hr
D= diameter of orifice hole, in
Δh= pressure drop across one plate, ft liquid

- In general , the ratio of pipe area to the total orifice area may range from 3 to 10 .
- The feet of liquid may be converted to pounds per square inch by

Psi = (ft of fluid) * (Spg) * (0.433)

Or

$$\text{Psi} = \frac{\text{Ft of fluid}}{2.148 + 0.01623\ (\text{API})}$$

Example : Acid is to be mixed with 8000 Bbl per day of 53 API pressure distillate. A pressure drop of 25 psi is permissible. If pressure drop across one plate is 5.5 ft liquid, design the orifice mixer.

Given that the pipe area= 3 – 10 orifice area.

Solution:

$$\text{Bbl per hr} = \frac{8000\ \text{Bbl / day}}{24\ \text{hr/day}} = 334$$

$$334 = 17.8\ D^2\ \sqrt{5.5}$$

D = 2.83 in diameter of orifice hole

$$A = \frac{\pi}{4} D^2 = 6.3\ \text{in}^2$$

if 7/8 in holes is used how many holes required per plate

$$\underset{\text{per plate}}{\Delta\ \text{psi}} = \frac{\text{ft of fluid}}{2.148 + 0.01623\ (\text{API})}$$

$$= \frac{5.5}{2.148 + 0.01623 * (53)} = 1.83$$

$$\text{No. of plates} = \frac{25}{1.83} = 14 \text{ plates}$$

for 1 ft spacing, H = 16 ft

pipe area= 3 – 10 orifice area

pipe area = 5*6.3 = 31.5 in ^{2}

pipe diameter = 6.3 in

use standard pipe of 6 in with A= 28.9 in^2 , use clearance of 1/16 in

12 7/8 in holes total opening = 7.64 in ^{2}

Settlers or Separators :

- In general caustic and water mixtures are rapidly settles,
- 10- 30 minutes are used as settling time.
- The settlers are usually 40 ft high and 2- 10 ft diameter.
- The velocity of the fluid in the settler should not exceed about 3 ft/ min.
- Stockes law governs the rate of settling.

Example : Design a settler to handle the separation of caustic from 12000 bbl of oil per day.

Solution:

Assume 30 min settling time

$H = 40$ ft

$$\text{Volume of oil per hr} = \frac{12000 * 42}{24 * 7.5} = 2800 \text{ ft}^3$$

$$\frac{2800}{2} = 1400 \text{ ft}^3 \text{ handled in 30 min}$$

$$A = \frac{1400}{40} = 35 \text{ ft}^2$$

$D = 6$ ft $= 10$ in

If 40 ft tank are not convenient, use two 20 ft tanks connected in series

$$v = \frac{gD^2(\rho_s - \rho_l)}{18\mu}$$