Lecture 7

Petrochemicals Engineering

Gas Sweetening Process

Sour gas

- High content of sulphur gas (H2S) and carbon dioxide (CO2)
- Acid gasses forms acid in the presence of H2O

$H_2S + H_2O \rightarrow H_3O^+ + HS^-$; $HS^- + H_2O \rightarrow H_3O^+ + S^-$

$CO_2 + H_2O \rightarrow H_2CO_3$

- Gas sweeting process
  - Decreases sulphur content of a gas
  - The unit operation of gas sweeting is absorption operation.
  - Amine gas treating solvents:
    - Diethanolamine (DEA)
    - Monoethanolamine (MEA)
    - Diisopropylamine (DIPA)
    - Aminoethoxyethanol (Diglycolamine) (DGA)
    - Diglycolamine

Gas x + L ⟶ Lx + gas

Table 1-3 Gases removed by various processes

Process	GASES REMOVED				
	CO_2	H_2S	RHS	COS	CS_2
Solid Bed					
Iron sponge		X			
Sulfa-Treat		X			
Zinc Oxide		X			
Molecular Sieves	X	X	X	X	X
Chemical Solvents					
MEA—MonoEthanolAmine	X	X		X[a]	X
DEA—DiEthanolAmine	X	X		X	X
MDEA—MethylDiEthanolAmine		X			
DGA—DiGlycolAmine	X	X		X	X
DIPA—DiIsoPropanolAmine	X	X		X	
Hot potassium carbonate	X	X		X	X
Physical Solvents					
Fluor Solvent	X	X	X	X	X
Shell Sulfinol®	X	X	X	X	X
Selexol®	X	X	X	X	X
Rectisol		X			
Direct Conversion of H_2S to Sulfur					
Claus		X			
LO-CAT®		X			
SulFerox®		X			
Stretford		X			
Sulfa-Check		X			
Nash		X			
Gas Permeation	X	X			

[a]MEA reacts nonreversibly with COS (carbonyl sulfide), and, therefore, should not be used to treat gases with a large concentration of COS.

- Natural gas : sour gas and sweet gas
- Acid gases: H_2S, CO_2 , COS and Mercaptans
- Environmental concern: Acid rain, Green house gas and criteria pollutants.
- The H_2S and CO_2 in the natural gas well streams are called Acid gases because they form acids or acidic solutions in the presence of water.
- They have no heating value and cause proplems to systems and the environment.
- H_2S is a toxic, poisonous gas and can not be tolerated in gases that they may be used for domestic fuels.
- H_2S in the presence of water is extremely corrosive and can cause premature failure of values, pipeline and pressure vessels.
- It can also cause catalyst poisoning in refinery vessels and requires expensive precautionary measures.
- Most pipeline specifications limit H_2S content to 0.25 g/100 ft^3 of gas about 4 ppm .

Sweetening process

Solid bed
- The iron sponge process
- Molecular sieve

Absorption

Direct conversion
- Stretford process

physical absorption process
- Water wash process
- Selexol process
- sulfinol process

Chemical absorption process
- Alkanol amine process
- Hot potassium carbonate

❖ Hydrogen sulfide removal process

A- Absorption by regenerative solvent (wet process)
- chemical solvents (Amines, Carbonates)
- Physical solvents (Di-methyl ether).
- Hydrid solvents.

B- Absorption on solid bed (dry process
- Non- Regeneration (Zinc and Iron oxide)
- Regeneration adsorbent (Molecular sieve)

❖ Membranes

Removal of H2S

- Girbotol process (Amine process)
  - MEA, DEA, DGA, MDEA etc.,
- Refined corporation (Carbonates)
  - K2CO3
- Selexol (Acid gas removal)
  - physical solvents (MPEG)

- ✓ Non-regenerative
- ✓ Regenerative Processes with recovery of H_2S
- ✓ Regenerative Processes with recovery as elemental Sulfur

- ✓ Elemental sulfur recovery
  - ✓ Claus processes
    - ✓ *Modified Claus process (reaction equilibrium limited)*
    - ✓ *Cold bed adsorption process*
    - ✓ *Modified Claus process with tail gas clean up*
  - ✓ Selective oxidation (Parson's Hi Activity process)
    - ✓ Iron based metal oxide catalyst
  - ✓ Wet oxidation based on aqueous solution (redox)
  - ✓ Thermal cracking of H_2S

Removal of Mercaptanes

- Caustic treatment (lighter Mercaptanes)
- Mer-ox processes
  - Mervx extraction
  - Mervx sweeting
- Mercaptanes to disulfides.
  - doctor sweeting (Na2PbO2)

- Cryogenic fractionation
- Biological process

Hybrid process

PSA process

Iron-sponge sweeting

Is a batch (dry box) process with the sponge being hydrated iron oxide (Fe2O3) supported on wood shavings.

The reaction between the sponge and H2S

$$2\,Fe_2O_3 + 6H_2S \rightarrow 2\,Fe_2S_3 + 6H_2O$$

- Regeneration reaction

$$2\,Fe_2S_3 + 3\,O_2 \rightarrow 2\,Fe_2O_3 + 6S$$

- The ferric oxide is present in a hydrated form.
- The reaction does not proceed without the water.
- The reaction requires the temperature < 120 F.

- The number of re-generation steps is limited due to the sulfur remaining in the bed and the beds have to be replaced.

Sweetening of Natural Gas

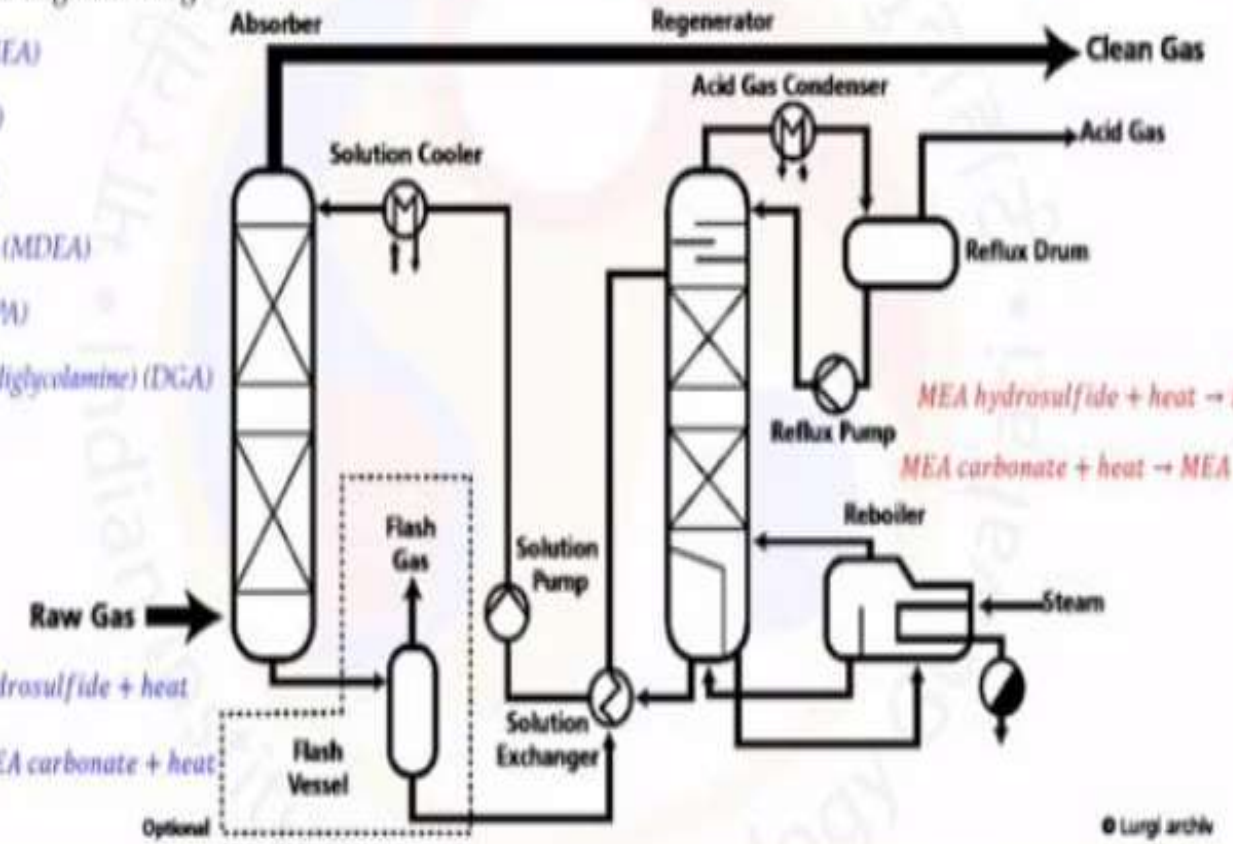
Amine based sweetening process

Alkanolamine Sweetening

is not selective and must be designed for total acid-gas removal

Different amines used in gas treating:

- *Monoethanolamine (MEA)*
- *Diethanolamine (DEA)*
- *Triethanolamine(TEA)*
- *Methyldiethanolamine (MDEA)*
- *Diisopropylamine (DIPA)*
- *Aminoethoxyethanol (diglycolamine) (DGA)*



$MEA + H_2S \rightarrow MEA\ hydrosulfide + heat$

$MEA + H_2O + CO_2 \rightarrow MEA\ carbonate + heat$

$MEA\ hydrosulfide + heat \rightarrow MEA + H_2S$

$MEA\ carbonate + heat \rightarrow MEA + H_2O + CO_2$

Sulfinol Process

to remove H_2S, CO_2, COS, CS_2, mercaptans and polysulfides from natural gas
process flow sheet is similar to Amine process

- ✓ uses a mixture of solvents allowing it to behave *as both a chemical and physical solvent process.*
- ✓ solvent is composed *of sulfolane* (physical solvent) *diisopropanolamine (DIPA,* chemical solvent, *and water.*
- ✓ is usually used for higher H_2S/CO_2 ratio or where CO_2 removal is not required to the same extent as H_2S.

- The main advantages of Sulfinol are:
  - low solvent circulation rates, low vaporization losses of the solvent
  - low degradation rates; low corrosion rates, low foaming tendency
  - *high effectiveness for removal of carbonyl sulfide, carbon disulfide, and mercaptans*

- 40 % Sulfolane
  (a physical solvent)
- 20 % water and
- 40 % DIPA or MDEA
  (both chemical solvents)

Some of the disadvantages of sulfinol include absorption of heavy hydrocarbons and aromatics

Criteria process selection

- The type and concentrations of the impurities in the gas and the degree of removal desired.
- CO_2 to H_2S ratio in the gas.
- Selectively of the acid gas removal, if any.
- Temperature and pressure at which the sour gas is available and which the sweet gas is be delivered
- Volume of the gas to be processed and its hydrocarbon composition.
- Economics of the process.
- The desirability of the s-removal; due to environmental problems or economics.

- Inlet gas knockout
- absorber
- Flash tank
- heat exchanger
- regenerator
- Filtration

Thank you