Gas Processing and Liquefaction

Chapter 4:
Hydrocarbon Gas Conditioning
Topic Outcomes:

- Name and explain the most common types of acid-type contaminants and its effects for hydrocarbon gas production, transportation, and utilization
- Define the common terms of hydrocarbon gas sweetening process
- Explain the need for hydrocarbon gas sweetening
- Describe the most common hydrocarbon gas sweetening methods that include chemical-and physical solvent based processes, and perform related engineering calculations
- Describe the other acid gas removal processes that include adsorption and gas permeation, and perform related engineering calculations
- Explain the process that can convert undesired hydrogen sulfide into a valuable product
Contaminants in Hydrocarbon Gas Flow

• Natural gas well streams often contain undesirable contaminants such as ammonia (NH₃), hydrogen sulfide (H₂S), hydrogen cyanide (HCN), carbon dioxide (CO₂), carbonyl sulfide (COS), carbon disulfide (CS₂), mercaptans (RSH), nitrogen (N₂), water (H₂O), sulfur dioxide (SO₂), elemental sulfur, mercury, arsenic and oxygen.

• Removal of these contaminants is required for:
  • reason of safety
  • corrosion control
  • gas and/or liquid product specification
  • to prevent freeze-out at low temperature
  • to decrease compression cost
  • to prevent poisoning of catalysts in downstream facilities
  • to meet environmental requirements
The removal of water (dehydration) was already discussed in the previous chapter.

This topic will only deal with removal of some or all of the sulfur-containing compounds and carbon dioxide.

Some definitions of words;

- **Acid gases** = Impurities in a gas stream usually consisting of CO2, H2S, COS, RSH, and SO2. Most common in natural gas are CO2, H2S and COS.

- **Sour gas** = Gas containing undesirable quantities of hydrogen sulfide, mercaptans and/or carbon dioxide

- **Mercaptans** = Any of a homologous series of compounds of the general formula RSH. Example: methyl mercaptan

- **Sweet gas** = Gas which has no more than the maximum sulfur content defined by: (1) the specifications for the sales gas from a plant, (2) the definition by a legal body
GPP Overview Block Diagram...A review

**FEED PRETREATMENT UNIT**
1. Removal of solid contaminants from gas & liquid
2. Separated entrained liquid from gas feed
3. Chloride removal from gas feed

**DEHYDRATION & REGENERATION UNIT**
1. To remove H2O & mercury from gas feed
2. To prevent hydrate formation and mercury in low temperature separation unit

**LOW TEMPERATURE SEPARATION UNIT**
1. Cool down feed gas in a series of aluminium heat exchangers and cryogenic refrigeration
2. To strip methane and lighter components as sales gas from demethanizer

**ACID GAS REMOVAL UNIT**
To remove carbon dioxide below 2000 ppmv, H2S and mercaptan in feed gas using Benfield Solution

**SALES GAS COMPRESSOR UNIT**
To compress of sales gas to meet the battery limit pressure

**PRODUCT RECOVERY UNIT**
To remove C2, C3, C4 and C5 from overhead and bottom of fractionators respectively

**REFRIGERATION UNIT**
A propane closed loop refrigeration unit to provide required cooling duty

**UTILITIES SECTION**
1. Steam system
   - HP Steam (40 barG, 370 degC)
   - MP Steam (17 barG, 220 degC)
   - LP Steam (6.5 barG, 185 degC)
   - LLP Steam (3.5 barG, 155 degC)
2. Fuel Gas
   - LP Fuel (2.5 barG)
   - MP Fuel (21 barG)
3. Nitrogen Gas (6.5 barG)
4. Cooling Water (4.5 barG)
Acid Gases in Natural Gas Flow

• H₂S and CO₂ are the main acid gases which have to be removed from natural gas. It is usually desirable to remove both H₂S and CO₂ to prevent corrosion problems and other operational problems, as well as to increase heating value of the gas.

• H₂S
  • Toxic and very poisonous
  • Extremely corrosive with the presence of water
  • Can cause catalyst poisoning in refinery vessels

• CO₂
  • Gas with no heating value
  • Corrosive with the presence of water
  • If gas is going to cryogenic plants, presence of CO₂ may cause solidification
Acid Gases in Gas Flow Cont..

- **Gas conditioning or treating** is usually referred to the process of removal of sulphur compounds and CO2 from natural gas.
- **Gas sweetening** is referred to a process of removal of sulphur compounds: e.g. H2S, carbon disulfide (CS2), carbonyl sulfide (COS) and mercaptans.
- Both gas sweetening and treating are generally referred to the process of removing or **actually** reducing the amount of acid gases until to an acceptable limit. In gas processing plant (GPP), the process of removing/reducing acid gases contaminants will be handled by AGRU (Acid Gases Removal Unit).
- AGRU in GPP A which consists GPP 1, 2, 3 and 4 is based on UOP’s Benfield process while AGRU in GPP B (GPP 5 and 6) is operated using Amine process. Both are chemical absorption processes.
AGRU’s PFD

H_2O + K_2CO_3 + CO_2 = 2KHCO_3

FEED GAS WITH 0.2% CO_2
PRESS = 5943 kPa
TEMP = 104 C

2KHCO_3 = H_2O + K_2CO_3 + CO_2

CO_2 TO INCINERATOR
PRESS = 153 kPa
TEMP = 123 C

A2 201 (ABSORBER)
K_2CO_3 LEAN SOLUTION

FEED GAS WITH 9% CO_2

A2 202 (THERMAL REGENERATOR)

RICH SOLUTION
KHCO_3 + H_2O

FROM LEAN SOLUTION
FLASH TANK

RT2 201 AB

LEAK SOLUTION
K_2CO_3

LLP STEAM
T2 204
AGRU in GPP A
Sweetening of natural gas is one of the most important steps in gas processing for the following reasons:

- **Health hazards**: At 0.13 ppm, H2S can be sensed by smell. At 4.6 ppm, the smell is quite noticeable. As the concentration increases beyond 200 ppm, the sense of smell can cause fatigue, and the gas no longer be detected by odor. At 500 ppm, breathing problems are observed and death can be expected in minutes. At 1000 ppm, death occurs immediately.

- **Sales contracts**: One of the most important natural gas pipeline specification are related to sulfur content. Such contracts depend on negotiations, but they are strict about H2S content.

- **Corrosion problems**: If the partial pressure of CO2 exceeds 15 psia, inhibitors usually can only be used to prevent corrosion. The partial pressure of CO2 depends on the mole fraction of CO2 in the gas and the natural gas pressure. Corrosion rates will also depend on temperature. Special metallurgy should be used if CO2 partial pressure exceeds 15 psia.
Acid Gases Removal Process: Selection

Factors

• Many factors must be considered in selecting an acid gas removal process including:
  • Natural gas composition
  • Acid gas content of the gas to be processed and selectivity required for acid gas removal
  • Final specifications of the product
  • Gas throughput to be processed
  • Temperature and pressure at which the sour gas is available and at which the sweet gas must be delivered
  • H2S removal conditions with or without sulfur recovery
  • Acid gas disposal method or environmental consideration
  • Relative economics which include capital cost, operating cost and royalty cost for process

• Basically, the processes of removing/reducing acid gases contents can be classified as below;
  i) By absorption based on Chemical Solvents
  ii) By absorption based on Physical Solvents
  iii) By adsorption
  iv) By gas permeation
Process Selection Chart for Simultaneous Removal of $\text{H}_2\text{S}$ and $\text{CO}_2$
Acid Gases Removal Processes Based on Chemical Solvents

- Chemical reaction process involved in removing the H2S and/or CO2 from the gas stream. This process is so called “reactive separation”- acid gases are separated/removed (absorbed) by chemically reacting them with special solvents.
- The reaction may be reversible or irreversible.
- In reversible reactions, the reactive material (solvent) removes CO2 and/or H2S in the contactor (absorber column) at high pressure and low temperature. The reaction is reversed by high temperature and low pressure in the regenerator (stripper column).
- In irreversible processes, the chemical reaction is not reversed and removal of the acid gases requires continuous make up of the solvent.
- In general, there have two types of chemicals used as the solvents in these chemical absorption processes, which 1) aqueous alkanolamine or simply “amine”, 2) pottasium carbonate
Aqueous Amine Processes (Amine Scrubbing)

- GPP B use amine solvents currently in the AGRU system. It is originally applied to gas treating back in 1930, then has become the most widely used solvents for the removal of acid gases from natural gas streams.
- Triethanolamine (TEA) was the first used commercially for gas treating and sweetening.
- It has been displaced for conventional applications by other amines such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), diglycolamine (DGA) and methyldiethanolamine (MDEA).
- Amine processes are particularly applicable where acid gas partial pressure or low levels of acid gas are desired in the treated gas.
- Because of the water content of the solution minimizes heavy hydrocarbon absorption, these processes are well suited for gases rich in heavier hydrocarbons.
- Some amines can be used to selectively remove H2S in the presence of CO2
- Amines can be categorized into three classes; 1) Primary (RNH$_2$) such as MEA and DGA, 2) Secondary (R$_2$NH) such as DEA and DIPA, and 3) Tertiary (R$_3$N) such as TEA and MDEA
The following reactions are observed between $\text{H}_2\text{S}$ and a primary amine:

\[
2 \text{RNH}_2 + \text{H}_2\text{S} \rightleftharpoons (\text{RNH}_3)_2\text{S} \quad (7.13)
\]
\[
(\text{RNH}_3)_2\text{S} + \text{H}_2\text{S} \rightleftharpoons 2 \text{RNH}_3\text{HS} \quad (7.14)
\]

- $R$ demotes the functional group $\text{HOCH}_2\text{CH}_2$-
- Both reaction 7.13 and 7.14 are direct and fast. They also occur with other amines, but they are fastest with MEA.
- Amines also react with carbon dioxide by two types of reaction. In this case, primary amine reaction as below;
  
  a) Formation of carbonate and bicarbonate:
  
  \[
  2 \text{RNH}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons (\text{RNH}_3)_2\text{CO}_3 \quad (7.15)
  \]
  \[
  (\text{RNH}_3)_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_3\text{HCO}_3 \quad (7.16)
  \]
  
  b) Formation of carbonate:
  
  \[
  2 \text{RNH}_2 + \text{CO}_2 \rightleftharpoons \text{RNHCOONH}_3\text{R} \quad (7.17)
  \]
Chemistry

- Reactions (7.15) and (7.16) are slow because carbon dioxide must form carbonic acid with water (slow reaction) before reacting with amine.
- Reaction (7.17) which predominates with MEA, is relatively fast, and this is why, it is not possible to eliminate hydrogen sulfide selectively with MEA.
- By contrast, with tertiary amines, the reaction (7.17) is impossible.
- Generally, MEA and DEA are still widely used, but other amines which are introduced recently, such as DGA, DIPA and MDEA are arousing growing interest.
Typical PFD for Acid Gases Removal by Amine Scrubbing
Amines Used

- MEA – Gas sweetening with MEA is used where there are low contactor pressure and/or stringent acid gas specifications. MEA removes both H2S and CO2 from gas streams.
  - H2S concentrations well below 4 ppmv can be achieved and CO2 can be as low as 100 ppmv (at low to moderate pressure).
  - Total acid gases pick up are traditionally limited to 0.3-0.35 moles of acid gases/mole of MEA and solution concentration is usually limited to 10-20 wt%.
  - Because MEA has the highest vapor pressure of the amines used, solution losses thru vaporization from the contactor and stripper can be high. This problem can be minimized by using a water wash.

- DEA – Helps to overcome the limitation of MEA, and can be used in the presence of COS and CS2
  - Among the process using DEA is the SNPA-DEA process developed by TOTAL.
Amines Used Cont..

- DIPA – used in relatively high concentrations from 30 to 40% of solvent, and it was developed by Shell
  - The applications mainly concern the processing of refinery gas (or liquids) containing COS
  - Also used in mixtures with physical solvents, such as sulfolane and water in the Sulfinol process
- DGA – is a primary amine capable of removing not only H2S and CO2, but also COS and mercaptans from gas and liquid streams.
  - Used in GPP and Refinery plants. DGA has greater affinity for the absorption of aromatics, olefins and heavy hydrocarbon than MEA and DEA systems.
  - As compared to MEA system, DGA can reduce reboiler steam consumption and higher acid gases pick-up per gallon of amine used.
MDEA- tertiary amine allows the selective absorption of H2S in the presence of CO2
- As it is highly selective for H2S and easier to regenerate than MEA and DEA, it has become the industry’s standard for selective treating application.

- Amine solutions are basic and hence non-corrosive. They are in fact used as corrosion inhibitors.
- In the presence of sour gases, however, significant corrosion is liable to occur at points where the temperature and concentration of the sour gases are high. The primary amine is the most corrosive.
- Foaming is a frequent problem in these amine processes. This is due to many causes:
  i) Suspended solids
  ii) Condensed hydrocarbons
  iii) Amine-degradation products
  iv) Foreign matter from corrosion inhibitors, from grease or from contaminants in the water
Pottasium Carbonate Scrubbing

• The pottasium carbonate scrubbing process in Fig 7.26 is similar to an amine process, but the solvent more concentrated 20 to 40% wt
• It was originally intended to remove CO2, but H2S is also absorbed.
• Absorption by a “hot” pottasium carbonate considerably boosts the absorption rate.
• The following chemical reactions are involved:
  i) $K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHC_3O_3 + \text{heat}$
  ii) $K_2CO_3 + H_2S \rightleftharpoons KHS + KHCO_3$
Pottasium Carbonate Scrubbing Cont..
(Experiences in GPP A)

- This process known as Benfield process (licensed by UOP) which to remove CO2 to less than 0.2% from up to 8% CO2 in the feed gas.
- Removal of CO2 by chemical absorption through Benfield solution. After absorption, this solution is stripped off from CO2 in the regenerator and the solution (solvent) is pumped back to the absorber.
- Benfield solution is a mixture of 30%wt pottasium carbonate, 3% DEA (activator), 0.5% vanadium pentoxide (corrosion inhibitor), 200 ppm of antifoam and the balance is H2O.
- The Benfield process is a thermally regenerated cyclical solvent process that uses an activated, inhibited hot potassium carbonate solution to remove CO₂, H₂S and other acid gas components. The high temperature operation of the Benfield process prevents hydrocarbon condensation from occurring.
Pottasium Carbonate Scrubbing Cont. (Experiences in GPP A)

- Some of the operational problems in this unit:
  1. Higher slippage of CO2 from the absorption tower, because of higher amount of CO2 in the feed (higher amount of CO2 vs absorption capacity)
  2. Foaming, because of solids particles suspended in solution and heavier hydrocarbons that condense in solution
  3. Corrosion, because of DEA degradation, existence of soluble metal and insufficient amount of vanadium pentoxide as corrosion inhibitor
## Foam Test Interpretation

<table>
<thead>
<tr>
<th>Foam Height (cm)</th>
<th>Interpretation and Action Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 2 cm</td>
<td>Pure water / clean solution</td>
</tr>
<tr>
<td>2 – 4 cm</td>
<td>Normal operating solution, non foaming</td>
</tr>
<tr>
<td>5 - 6 cm</td>
<td>Slightly foaming, monitor closely</td>
</tr>
<tr>
<td>7-10 cm</td>
<td>Solution is foaming, start injecting antifoam</td>
</tr>
<tr>
<td>10 – 15 cm</td>
<td>Heavy foaming, rapid antifoam injection Reduce gas and solution circulation</td>
</tr>
</tbody>
</table>
Class Discussion on:

- Acid gases removal by absorption using physical solvents
- Acid gases removal by adsorption
- Acid gases removal by gas permeation
- Acid gas fractionation
- Conversion of hydrogen sulfide to sulfur
- Removal of nitrogen and helium
- Removal of mercury
Membrane Process in General

- Membrane is a semi-permeable barrier to create a separation by controlling the rate of movement of species between two phases.

- The separation can involve:
  - Two gas (vapor) phases
  - Two liquid phases
  - A vapor and liquid phase

- The feed mixture is separated into a *retentate* and a *permeate*.
  - *Retentate: the part of the feed that does not pass through the membrane*
  - *Permeate: the part of the feed that passes through the membrane*

- The driving forces
  - Gas or vapor: partial pressure
  - Liquid: concentration
    - Normally created by the imposition of a pressure different across the membrane
    - For liquid separations: also created by the use of solvent or an electrical field
Classification of Membrane Processes

- The most important membrane separation processes are classified into:
  - Gas permeation (with complete-mixing model is our focus!)
  - Gas diffusion in porous solid
  - Liquid permeation or dialysis
  - Reverse osmosis
  - Ultra-filtration membrane process
  - Microfiltration membrane process
  - Gel permeation chromatography
Gas Permeation

- Lower molecular weight species are separated from higher weight species
- A high pressure gradient across the membrane
  - The feed is at high pressure and the other side of the membrane at a low pressure
  - Typically in the range of 20 to 40 bar
- Typical applications of gas permeation include:
  - Removal of CO2 and H2S from natural gas (our focus!)
  - Separation of hydrogen from methane
  - Air separation
  - Helium recovery from natural gas
  - etc