**Syngas Clean Up**

In most cases the gas must be cooled to atmospheric, with the exception of the desulfurization which may have ways of being performed at higher temperatures. The four main processes involved in gas clean up are:

• Absorption (physical or chemical) in a liquid solvent with a subsequent desorption step.

• Adsorption (again physical or chemical) onto a mass of solid particles.

• Diffusion through a permeable or semipermeable membrane.

• Chemical conversion, generally on a catalyst, often as a preparatory step to one of the above three methods.

(Higman, page 298)

It is important to pick the proper processes to ensure that the cleanest syngas is produced at the end of all the cleaning. Most particulates in the dirty gas can be removed through physical processes. In the absorption system the acid components are removed through the use of solvents and regenerating those solvents to remove the unwanted components so it then can be reused in the absorber. The main purpose here is to remove the H2S and CO2 from the dirty syngas. There are many solvents available for this application, plus there are multiple processes that are implemented to clean the acid gas.

Amines are used as a chemical wash with water to clean the acid gases.

“The principle amines used for synthesis gas treatment are mono- and diethanolamine (MEA and DEA), methyldiethanolamine (MDEA), and di-isopropanolamine (DIPA), the latter particularly as a component of the Sulfinol solvent. Others amines used in natural gas applications, such as diglycolamine (DGA) or triethanolamine (TEA), have not been able to make any significant impact in syngas applications” (Higman, page 301).

The selection of the amine can be based off of how selective it is with H2S and CO­2, for example MDEA absorbs CO2 more slowly than H­2S. A table comparing this can be found in the Gasification book by Higman on page 302 which is below as table 1.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Properties of Amine Solvents** | | | | |
|  | **Standard MEA** | **Inhibited MEA** | **DEA** | **MDEA** |
| **Molecular Weight** | 61 |  | 105 | 119 |
| **CO2 partial pressure (bar)** | <100 | <100 |  |  |
| **Gas Purity CO2 (ppmv)** | 20-50 | 20-50 |  |  |
| **Solution Strength (wt%)** | 10-20 | 30 | 25-35 | 30-50 |
| **Solution Loading (mol/mol)** | 0.25-0.45 |  | 0.4-0.8 | 0.8 |
| **Energy Demand (MJ/kmol CO2)** | 210 | 140 |  |  |
| **Notes:** |  |  |  | Selective |

**Table 1: Properties of Amine Solvents (Higman, page 302)**

There are also physical washes that can be used in the acid gas separations because they have a good solubility with CO2, H2S, and COS and work at lower operating temperatures where the viscosity is increased and can be adjusted to affect the overall solubility (Higman, page 303). A table of these physical solvent properties can be found in the Gasification book by Higman on page 304 which is shown below as table 2.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Properties of Physical Solvents** | | | | |
|  |  | **Methanol** | **NMP** | **DMPEG** |
| **Chemical Formula** |  | CH3OH | CH3N-(H2C)3  C=O | CH3O(C2H4O)X  CH3 |
| **Mol. Weight** | Kg/kmol | 32 | 99 | 178 to 442 |
| **Boiling Point at 760 Torr** | °C | 64 | 202 | 213 to 467 |
| **Melting Point** | °C | -94 | -24.4 | -20 to -29 |
| **Viscosity** | cP | 0.85 at -15°C  1.4 at -30°C  2.4 at -50°C | 1.65 at 30°C  1.75 at 25°C  2.0 at 15°C | 4.7 at 30°C  5.8 at 25°C  8.3 at 15°C |
| **Specific Mass** | Kg/m3 | 790 | 1.027 | 1.031 |
| **Heat of Evaporation** | kJ/m3 | 1090 | 533 |  |
| **Specific Heat at 25°C** | kJ/kg.K | 0.6 | 0.52 | 0.49 |
| **Selectivity at working temperature** | (H2S:CO­2) | 1:9.5 | 1:13 | 1:9 |

**Table 2: Properties of Physical Solvents (Higman, page 304)**

In the case of our system we will most likely have to use a mixture of the two, which is appropriately named physical-chemical washes. Shell has produced a process using this method with a special chemical called Sulfinol (Higman, page 307). The original Sulfinol mix consisted of DIPA (the chemical solvent) and Sulfolane (the physical solvent). There is also m-Sulfinol solvent that uses MDEA as its chemical component (Higman, page 307). M-Sulfinol is used for larger scale processes such as our own.

Oxidative washes (aka liquid redox) are an alternative to the Claus plant to remove the H2S into elemental sulfur. However this process will only convert the H2S so therefore the COS must be converted upstream to H2S to obtain a better purity in the end. Below is the figure from form Gasification on page 308 which shows a basic process flow of the Lo-Cat process that converts the acid gas into elemental sulfur be being absorbed on aqueous chelated iron. The ferric iron oxidizes the HS- ion to elemental sulfur. Further on down the process path a bed of zinc oxide and also copper oxide can be used to ensure the remaining gas is as sulfur free as possible.



Figure 1: Lo-Cat Flowsheet (Higman, page 308)

The Claus process is another method in removing the sulfur content from the syngas. The H2S is combusted with SO­2 and water in the first stage at 1000-1200°C (1832-2192°F) where then the in the low-temperature second stage the SO2 is reacted with the remaining H2S to form sulfur (Higman, page 319-320).



Figure 2: Claus Unit (Higman, page 319)

In the second stage the gas is passed over and alumina catalyst at around 200-300°C (392-572°F) where is then sent to a cooler to condense the sulfur formed (Higman, page 319). This usually is performed two to three times, and in the case of our process it is most likely that we will perform this three times to ensure the most sulfur can be removed.