Tikrit University

College of Petroleum Processes Engineering

Department of Petroleum and Gas Refining Engineering

Gas Technology

Forth Class

Lecture 13

By

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ACID GAS TREATING

1. Batch Type Processes

1.1. Metal Oxide Processes

1.1.1. Iron Sponge Process

1.1.2. Zinc Oxide Process

1.2. Slurry Processes

1.2.1. Chemsweet Process

1.2.2. Sulfa-Check Process
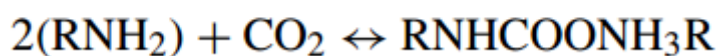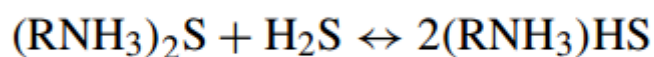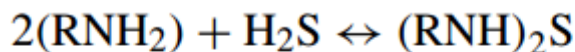
2. Amine Processes

- Chemical absorption processes with aqueous alkanolamine solutions are used for treating gas streams containing hydrogen sulfide and carbon dioxide. However, depending on the composition and operating conditions of the feed gas, different amines can be selected to meet the product gas specification.

- Amines are categorized as being primary, secondary, and tertiary depending on the degree of substitution of the central nitrogen by organic groups.

- **Primary amines** react directly with H_2S, CO_2, and carbonyl sulfide (COS). Examples of primary amines include monoethanolamine (MEA) and the proprietary diglycolamine agent (DGA).

- **Secondary amines** react directly with H_2S and CO_2 and react directly with some COS. The most common secondry amine is diethanolamine (DEA), while diisopropanolamine (DIPA) is another example of a secondary amine, which is not as common anymore in amine-treating systems.

- **Tertiary amines** react directly with H_2S, react indirectly with CO_2, and react indirectly with little COS. The most common examples of tertiary amines are
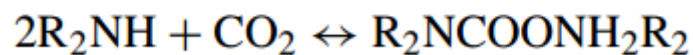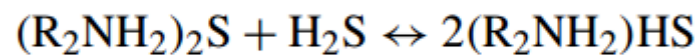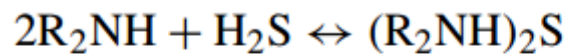
methyldiethanolamine (MDEA) and activated methyldiethanolamine. Processes using ethanolamine and potassium phosphate are now widely used. The ethanolamine process, known as the *Girbotol process*, removes acid gases (hydrogen sulfide and carbon dioxide) from liquid hydrocarbons as well as from natural and from refinery gases.

- The ethanolamine solution fills a tower called an absorber through which the sour gas is bubbled. Purified gas leaves the top of the tower, and the ethanolamine solution leaves the bottom of the tower with the absorbed acid gases. The ethanolamine solution enters a reactivator tower where heat drives the acid gases from the solution. Ethanolamine solution, restored to its original condition, leaves the bottom of the reactivator tower to go to the top of the absorber tower, and acid gases are released from the top of the reactivator.

- Amines with physical solvents, such as sulfolane and piperazine; and amines that have been partially neutralized with an acid such as phosphoric acid may also be used.

- MEA and DEA have found the most general application in the sweetening of natural gas streams. Even though a DEA system may not be as efficient as some of the other chemical solvents are, it may be less expensive. MEA is a stable compound and, in the absence of other chemicals, suffers no degradation or decomposition at temperatures up to its normal boiling point. MEA reacts with H_2S and CO_2 as follow:

$$2(RNH_2) + H_2S \leftrightarrow (RNH)_2S$$
$$(RNH_3)_2S + H_2S \leftrightarrow 2(RNH_3)HS$$
$$2(RNH_2) + CO_2 \leftrightarrow RNHCOONH_3R$$

These reactions are reversible by changing the system temperature.

- ↓ MEA also reacts with carbonyl COS and carbon disulfide (CS2) to form heat stable salts that cannot be regenerated. DEA is a weaker base than MEA and therefore the DEA system does not typically suffer the same corrosion problems but does react with hydrogen sulfide and carbon dioxide:

$$2R_2NH + H_2S \leftrightarrow (R_2NH)_2S$$

$$(R_2NH_2)_2S + H_2S \leftrightarrow 2(R_2NH_2)HS$$

$$2R_2NH + CO_2 \leftrightarrow R_2NCOONH_2R_2$$

- ↓ DEA also removes carbonyl sulfide and carbon dislduflide partially as its regenerable compound with COS and CS2 without much solution losses.
- ↓ The selectivity of MDEA-based products can lead to more energy savings. For example, allowing carbon dioxide to remain in the treated gas reduces the amount of acid gas in the amine that needs to be regenerated, thus reducing the amount of energy required. The use of MDEA for selective H2S removal is based on the fact that unlike DEA, MDEA does not react directly with CO_2.

2.1 Process Description

Figure 2 showed the general process flow diagram for an amine-sweetening plant.
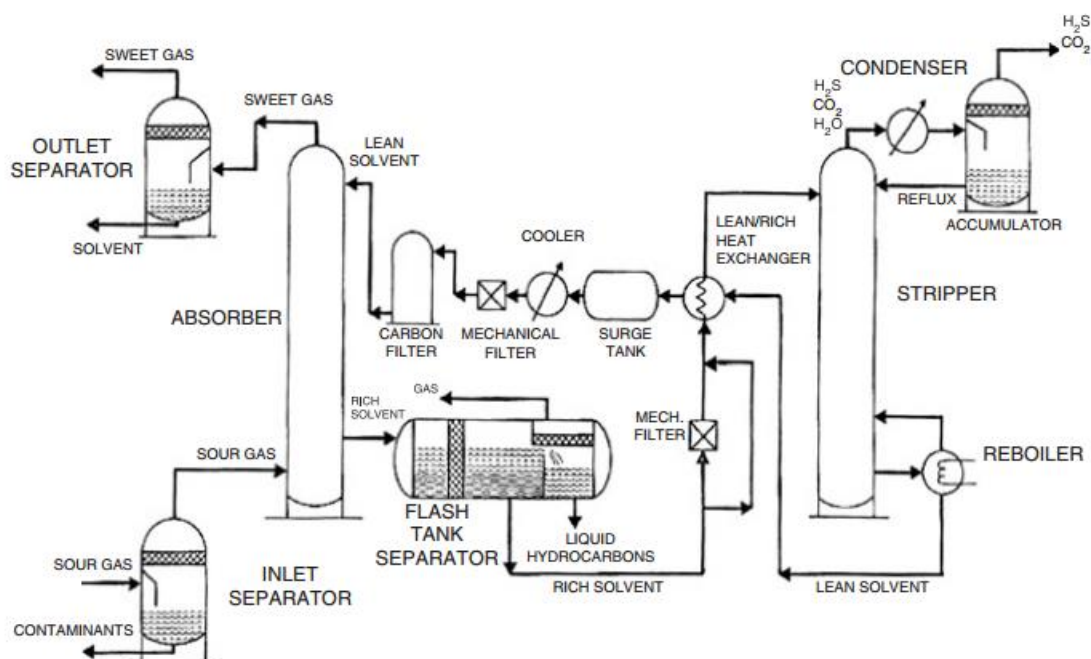
Figure 2: Schematic of amine gas-sweetening process flow diagram

- The sour gas containing H_2S and/or CO_2 will nearly always enter the plant through an inlet separator (scrubber) to remove any free liquids and/or entrained solids.

- The sour gas then enters the bottom of the absorber column and flows upward through the absorber in intimate countercurrent contact with the aqueous amine solution, where the amine absorbs acid gas constituents from the gas stream.

- Sweetened gas leaving the top of the absorber passes through an outlet separator and then flows to a dehydration unit (and compression unit, if necessary) before being considered ready for sale.

- In many units the rich amine solution is sent from the bottom of the absorber to a flash tank to recover hydrocarbons that may have dissolved or condensed in the amine solution in the absorber.

- The rich solvent is then preheated before entering the top of the stripper column. The amine–amine heat exchanger serves as a heat conservation device and lowers total heat requirements for the process. A part of the absorbed acid gases will be flashed from the heated rich solution on the top tray of the stripper. The remainder of the rich solution flows downward through the stripper in countercurrent contact with vapor generated in the reboiler. The reboiler vapor (primarily steam) strips the acid gases from the rich solution. The acid gases and the steam leave the top of the stripper and pass overhead through a condenser, where the major portion of the steam is condensed and cooled. The acid gases are separated in the separator and sent to the flare or to processing. The condensed steam is returned to the top of the stripper as reflux.

- The lean amine solution from the bottom of the stripper column is pumped through an amine–amine heat exchanger and then through a cooler before being introduced to the top of the absorber column. The amine cooler serves to lower the lean amine temperature to the 100◦F range. Higher temperatures of the lean amine solution will result in excessive amine losses through vaporization and also lower acid gas-carrying capacity in the solution because of temperature effects.

3. Carbonate Washing and Water Washing

Carbonate washing is a mild alkali process for emission control by the removal of acid gases from gas streams and uses the principle that the rate of absorption of carbon dioxide by potassium carbonate increases with temperature. It has been demonstrated that the process works best near the temperature of reversibility of the reactions:

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$$
$$K_2CO_3 + H_2S \rightarrow KHS + KHCO_3$$
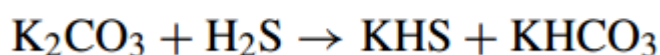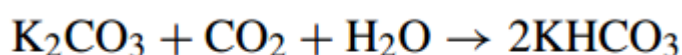
The absorption is purely physical and there is also a relatively high absorption of hydrocarbons, which are liberated at the same time as the acid gases.

4. Methanol Based Processes

- Methanol is probably one of the most versatile solvents in the natural gas processing industry.
- Operation at low temperatures tends to suppress the most significant disadvantage of methanol, high solvent loss. Furthermore, methanol is relatively inexpensive and easy to produce, making the solvent a very attractive alternate for gas processing applications.
- Methanol has low viscosity and much lower surface tension relative to the other solvents. However, the primary drawback of methanol is the high vapor pressure.
- To minimize methanol losses and enhance water and acid gas absorption, the absorber or separator temperatures are usually less than $-20 \circ F$.
- The use of methanol has been exploited further in the development of the **Rectisol process** either alone or as toluene–methanol mixtures are used to more selectively removes H_2S and slip CO_2 to the overhead product.

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Toluene has an additional advantage insofar as carbonyl sulfide is more soluble in toluene than in methanol.

- Unfortunately, at cold temperatures, methanol also has a high affinity for hydrocarbon constituents of the gas streams. For example, propane is more soluble in methanol than carbon dioxide. There are two versions of the Rectisol process: the two stage and the once through. The first step of the two-stage process is desulfurization before shift conversion; the concentrations of hydrogen sulfide and carbon dioxide are about 1 and 5 vol%, respectively. Regeneration of the methanol following the desulfurization of the feed gas produces high sulfur feed for sulfur recovery. The once-through process is only applicable for high-pressure partial oxidation products. The once-through process is also applicable when the hydrogen sulfide to carbon dioxide content is unfavorable, in the neighborhood of 1:50.

5. Other Processes

- The process using **potassium phosphate** is known as phosphate desulfhurization and is used in the same way as the **Girbotol process** to remove acid gases from liquid hydrocarbons as well as from gas streams. The treatment solution is a water solution of tripotassium phosphate (K_3PO_4), which is circulated through an absorber tower and a reactivator tower in much the same way as the ethanolamine is circulated in the Girbotol process; the solution is regenerated thermally.

- Other processes include the **Alkazid process** (Figure 3), which removes hydrogen sulfide and carbon dioxide using concentrated aqueous solutions of amino acids.

- The **hot potassium carbonate process** (Figure 4) decreases the acid content of natural and refinery gas from as much as 50% to as low as 0.5% and operates in a unit similar to that used for amine treating.

- The **Giammarco-Vetrocoke process** is used for hydrogen sulfide and/or carbon dioxide removal (Figure 5). In the hydrogen sulfide removal section, the reagent consists of sodium or potassium carbonates containing a mixture of arsenites and arsenates; the carbon dioxide removal section utilizes hot aqueous alkali carbonate solution activated by arsenic trioxide or selenous acid or tellurous acid.

- **Molecular sieves process** is highly selective for the removal of hydrogen sulfide (as well as other sulfur compounds) from gas streams and over continuously high absorption efficiency. They are also an effective means of water removal and thus offer a process for the simultaneous dehydration and desulfhurization of gas. Gas that has excessively high water content may require upstream dehydration, however. The molecular sieve process (Figure 6) is similar to the iron oxide process.

- Until recently, the use of **membranes** for gas separation has been limited to carbon dioxide removal. The new membranes are targeted at three separations: nitrogen, carbon dioxide/hydrogen sulfide, and natural gas liquids. The process uses a two-step membrane system design; the methane-selective membranes do not need to be operated at low temperatures, and capital and operating costs are within economically acceptable limits. For example, the membranes allow permeation of condensable vapors, such as C3+ hydrocarbons, aromatics, and water vapor, while rejecting the noncondensable gases, such as methane, ethane, nitrogen, and hydrogen. In another process, a membrane-based process for upgrading natural gas that contains C3+ hydrocarbons and/or acid gas is described.
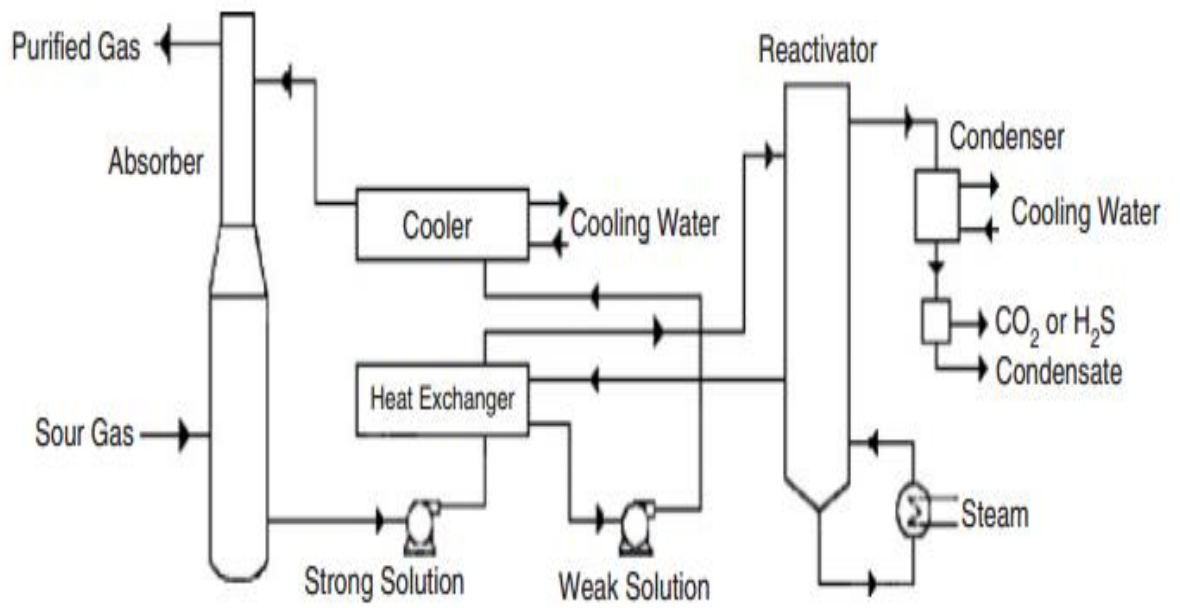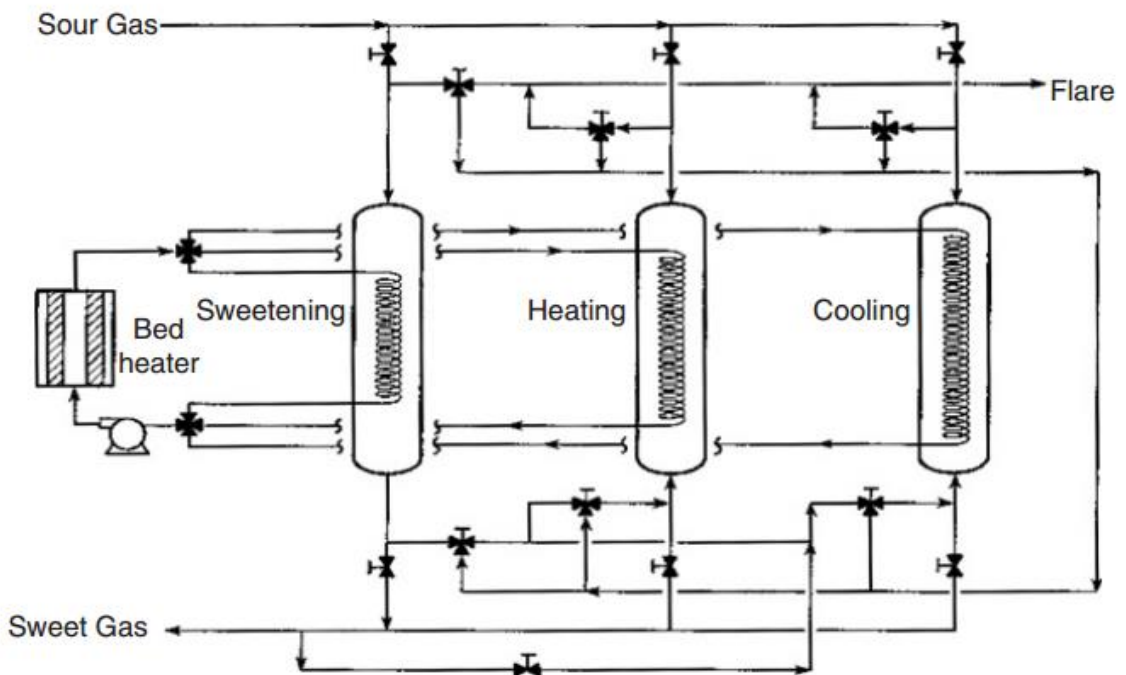
Figure 3: The Alkazid process flow diagram.
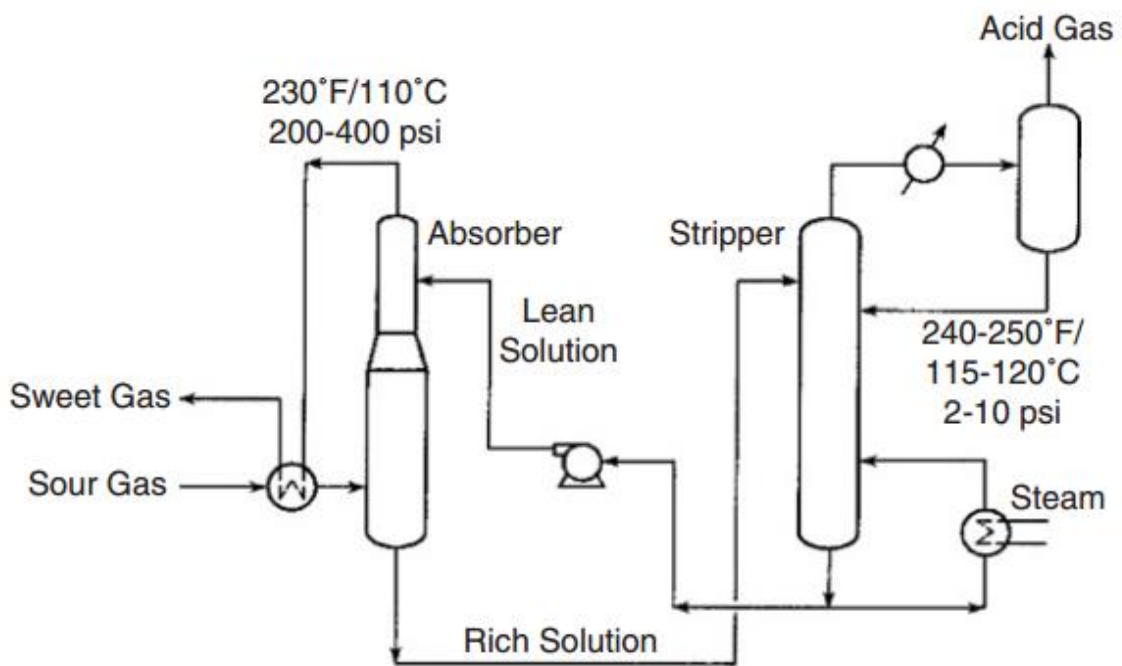
Figure 4: The hot potassium carbonate process flow diagram.
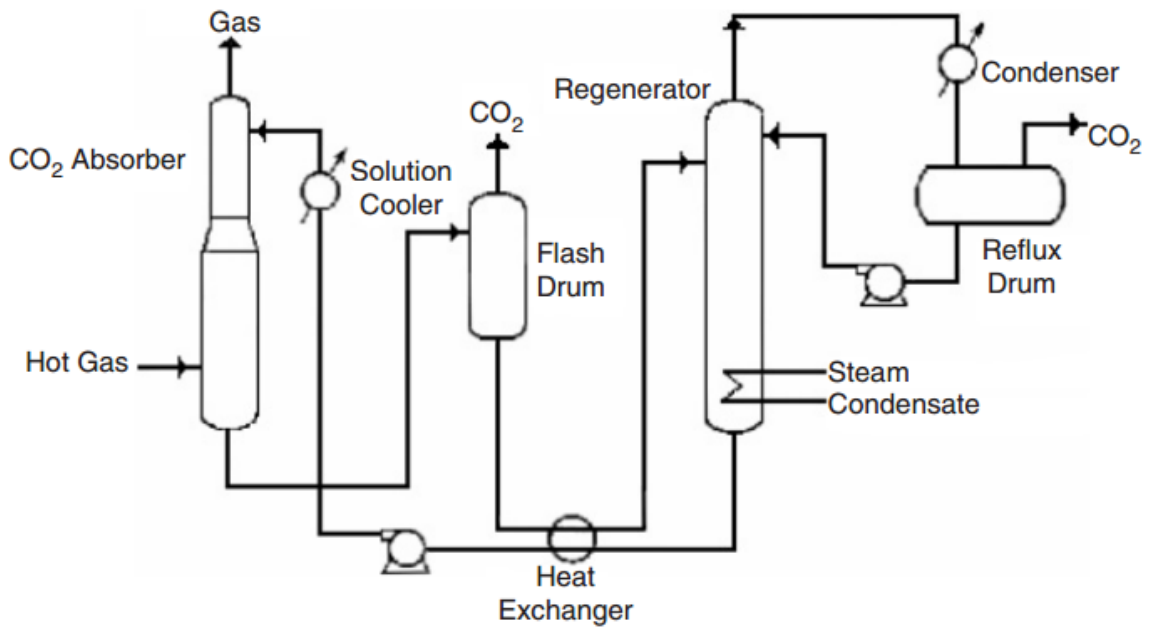
Figure 5: The Giammarco-Vetrocke process flow diagram

Figure 6: The molecular sieve process flow diagram

Process Selection

Each of the previous treating processes has advantages relative to the others for certain applications; therefore, in selection of the appropriate process, the following facts should be considered:

- Air pollution regulations regarding sulfur compound disposal and/or Tail Gas Clean Up (TGCU) requirements
- Type and concentration of impurities in the sour gas
- Specifications for the residue gas
- Specifications for the acid gas
- Temperature and pressure at which the sour gas is available and at which the sweet gas must be delivered
- Volume of gas to be processed
- Hydrocarbon composition of the gas
- Selectivity required for acid gas removal
- Capital cost and operating cost
- Royalty cost for process
- Liquid product specifications
- Disposal of by-products considered hazardous chemicals