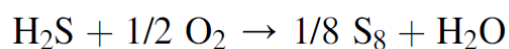


## 9. Sulfur Recovery and Handling

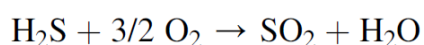
- ❖ **Acid gas** is a mixture of hydrogen sulfide ( $\text{H}_2\text{S}$ ) and carbon dioxide ( $\text{CO}_2$ ), with small amounts of hydrocarbon gases and usually water vapor.
- ❖ It is the by-product of the sweetening of **sour gas** and can be generated via any number of treating processes. If a nonaqueous solvent is used, then there may be a minimal amount of water in the acid gas stream.
- ❖ In the past, gas producers could flare/incinerate the acid gases; however, with growing environmental concerns from the emission of sulfur dioxide ( $\text{SO}_2$ ), the flaring of even small quantities of acid gas to the surroundings is generally unacceptable. This means that the hydrogen sulfide extracted from the acid gas removal unit must be further processed or must be injected downhole.
- ❖ Sulfur recovery refers to the conversion of  $\text{H}_2\text{S}$  to elemental sulfur. Hydrogen sulfide is a flammable gas with a wide limit of flammability and is extremely toxic. Elemental sulfur can be stored, handled, and transported in bulk.

### 9.1. Claus and modified Claus sulfur recovery process

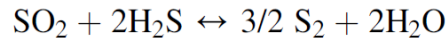
- ❖ In the original Claus process, elemental sulfur was produced by the partial oxidation of  $\text{H}_2\text{S}$  in a single step over a preheated catalyst bed, according to the following exothermic reaction:



- ❖ However, since the reaction was extremely exothermic, the original process was severely limited by the inability to control the reaction temperature, and consequently sulfur recovery was limited.
- ❖ In the **modified Claus** sulfur recovery process the overall reaction is carried out in two stages. In the first stage (thermal section), enough air is added to oxidize only one-third of the incoming  $\text{H}_2\text{S}$  to  $\text{SO}_2$ . This reaction is highly exothermic and is not limited by equilibrium.



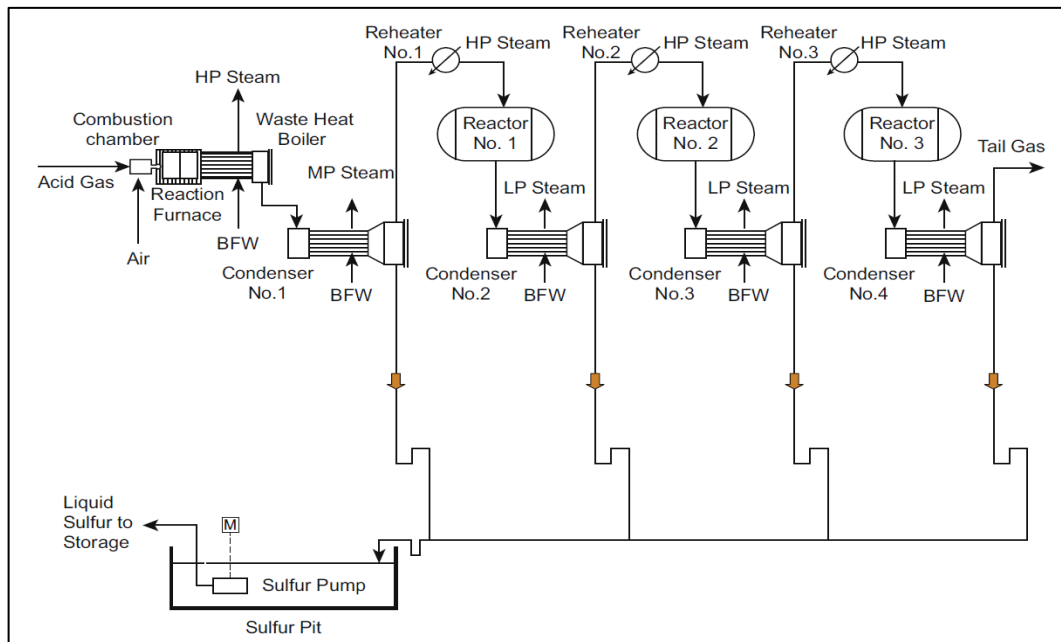
- ❖ In the reaction furnace the unburned  $\text{H}_2\text{S}$  in the acid gas reacts with the produced  $\text{SO}_2$  to yield elemental sulfur vapor. This reaction is referred to as the Claus reaction and is shown in Eq. below. This reaction is endothermic and is limited by equilibrium.



- ❖ Usually 60%-70% of the total conversion of  $\text{H}_2\text{S}$  to elemental sulfur is achieved in the thermal stage.

### 9.1.1 Process Description

A typical modified Claus process flow schematic is shown in Fig. below. In this process the overall reaction is carried out in two stages, **thermal and catalytic**.



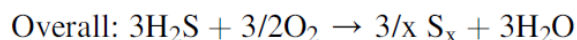
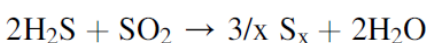
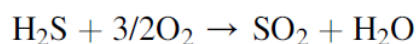
Typical process flow schematic of a once-through, three-stage Claus sulfur recovery unit. BFW, boiler feed water.

## 9.2. Direct Oxidation Processes

For lean acid gases that contain 5-30 mol %  $\text{H}_2\text{S}$ , the straight-through Claus process is not workable without additional equipment. The alternative is to replace the thermal section of the modified-Claus process by a direct oxidation process. There are several commercially proven processes including UOP's Selectox process and Linde's Clinsulf process, which are described in the following sections.

### 1. Selectox Process

UOP offers the Selectox process using their proprietary catalysts. Over the catalysts, air oxidizes  $\text{H}_2\text{S}$  to  $\text{SO}_2$  that reacts with additional  $\text{H}_2\text{S}$  to produce elemental sulfur, as shown in the following reactions.



The drawback of the catalytic process is the inability to handle contaminants such as hydrocarbons and aromatics, will react on the Selectox and Claus catalysts, causing hot spots and coke formation. Thus, the process is not as robust and forgiving as the thermal reactor in the Claus process. The Selectox units are generally smaller in capacities than the Claus units.

### 2. Clinsulf Process

Linde A.G. has developed a nonthermal, direct oxidation process called the Clinsulf process, which is typically applied to syngas operation. In the Clinsulf process,  $\text{H}_2\text{S}$  is directly oxidized to sulfur and  $\text{H}_2\text{O}$  in a reactor filled with a suitable catalyst. In this process the heat of reaction is removed directly from the Claus reactor with a coil-type tubular heat exchanger arranged within the catalyst bed. The internal cooling keeps the reaction temperature close to the sulfur dew point in order to maximize sulfur yield. A

single-stage Clinsulf unit claims to be capable of attaining up to 92% sulfur recovery for very lean acid gases ( $<5\%$   $\text{H}_2\text{S}$ ) and up to 95% for gases with 10%-20%  $\text{H}_2\text{S}$  content. With the cooling provided by the Linde reactor, it is theoretically possible to control the reaction temperature to below the sulfur dew point.

### 9.3. Tail Gas Cleanup

Tail gas from a Claus unit invariably contains small quantities of sulfur compounds whether it is from the conventional Claus process or its extended version. In earlier SRUs, removal of these trace quantities was not considered necessary since there were no strict regulations that limited sulfur emissions. However, as the air became more polluted, environmental regulations were imposed, and the unconverted sulfur emissions from the Claus unit tail gas became a target of regulation. This led to the development of Claus tail gas cleanup processes in order to remove the residual sulfur species to meet emissions regulations. Tail gas cleanup processes can be categorized into three general groups: **reduction,  $\text{SO}_2$  scrubbing, and catalytic oxidation.**

### 9.4. Sulfur Disposal by Acid Gas Injection (AGI)

- ❖ The acid gas stream, which is the by-product of the acid gas removal process, is normally sent to a sulfur recovery unit (SRU).
- ❖ However, if the acid gas contains more than about 60%  $\text{CO}_2$ , which is often the case with small amounts of  $\text{H}_2\text{S}$  in the sour natural gas, then a modified Claus plant may not be the best choice for small-scale sulfur recovery.
- ❖ It is somewhat difficult to operate, and the resulting sulfur product does not meet sulfur product purity specifications. In such situations, the best solution may be to compress the acid gas stream for disposal into depleted oil and gas reservoirs or into deep saline aquifers.
- ❖ In addition, injecting the acid gas stream into an underground formation is a viable process for gas processing plants located in remote locations where transport the sulfur product is not easy.

- ❖ This is also the only option if the gas plant is in an environmentally sensitive region, which mandates a zero emissions policy.

#### **9.4.1. Advantages and Disadvantages of AGI**

##### **Advantages**

1. an AGI unit is lower in capital and operating costs than a SRU, if the injection destinations are nearby, and especially if the injection wells can be converted from existing producing wells.
2. An AGI is less complex, making the unit easier to control and more reliable, if critical equipment is spared.
3. AGI systems can also easily handle wide ranges in the acid gas composition.
4. In addition, to providing a cost-effective alternative to sulfur recovery, the deep injection of acid gas may also help to maintain the oil field pressure, which enhances oil recovery and increases revenue.

##### **Disadvantages**

1. There are risks associated with handling hazardous gases at elevated pressures.
2. AGI processes are limited to cases where suitable injection reservoirs are available. If injected into an oil production reservoir, the sour gas will likely be reproduced at some point in the future.