

# MODIFIED CLAUS PROCESS APPLIED TO NATURAL GAS FOR SULFUR RECOVERY

Nicușor VATACHI, Viorel POPA

University "Dunărea de Jos" of Galati, ROMANIA

**Abstract:** *Approximately 25% of the natural gas being brought into production from new sources requires H<sub>2</sub>S removal and disposal. Consequently, sulfur removal processes will play an increasingly larger role in future gas processing. As late as 1950, over half of the world sulfur supply came from "voluntary producers," that is, companies whose principal purpose was to produce elemental sulfur. Now, these producers furnish less than 5% of the world's supply and "involuntary producers," primarily petroleum refineries and natural gas plants, are the major source of the element. The most common method of converting H<sub>2</sub>S into elemental sulfur, is the Claus process or one of its modifications. Unfortunately, the exit stream from Claus plants usually cannot meet environmental emission requirements, and, consequently, a tail gas cleanup unit (TGCU) is often employed to eliminate the last of the sulfur compounds. The most commonly used processes are Shell Claus off Gas Treating (SCOT), SUPERCLAUS, and cold-bed adsorption (CBA). This paper describes Claus and tail gas cleanup processes.*

**Keywords:** *sulfur recovery, gas processing, environmental protection, modified Claus process, tailgas cleanup processes.*

## 1. INTRODUCTION

Because approximately 25% of the natural gas being brought in to production from new sources requires H<sub>2</sub>S removal and disposal, sulfur removal processes will play an increasingly larger role in future gas processing. Currently only two methods are available for dealing with large quantities of H<sub>2</sub>S: disposal of the gas by injection into underground formations and conversion of the H<sub>2</sub>S into a usable product, elemental sulfur.

However, more commonly, H<sub>2</sub>S is converted into elemental sulfur, much of which goes into sulfuric acid production.

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The most common method of converting H<sub>2</sub>S into elemental sulfur is the Claus process or one of its modifications. Two modified

configurations are presented: straight-through and split flow:

- the straight-through process is the preferred and simplest. It can process feed streams that contain more than 55 mol% H<sub>2</sub>S; with air or acid gas preheat, and can process 30 to 55 mol% H<sub>2</sub>S in the feed;
- the split-flow configuration can process feeds that contain 5 to 30 mol% H<sub>2</sub>S. The straight-through process provides the highest sulfur-recovery efficiency.

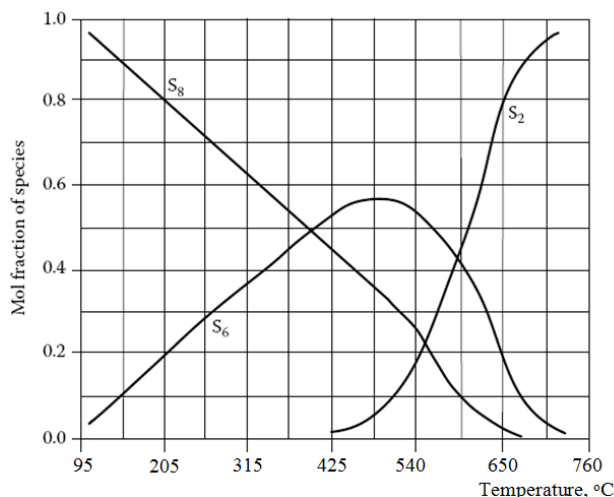
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## 2. PROPERTIES OF SULFUR

The thermo physical properties of sulfur are unusual. For a complete understanding of the Claus conversion process, a brief discussion of the relevant properties is necessary.

Sulfur vapor exists as  $S_x$ , where  $x$  can have values from 1 through 8. Figure 1 shows the distribution of sulfur-vapor species as a function of temperature.



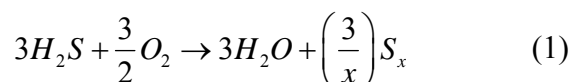
**Fig.1.** Sulfur-vapor species as a function of temperature.

Note that at lower temperatures,  $S_8$  dominates, but as the temperature rises  $S_8$  converts to  $S_6$ , and finally to  $S_2$ . The sequence is not unexpected, because increased temperature means increased energy for the molecules, which leads to the breakup of the clusters. The formation of sulfur clusters has a very pronounced effect on the physical properties that have a significant effect on processing operations, notably viscosity (fluid flow) and heat capacity (heat transfer).

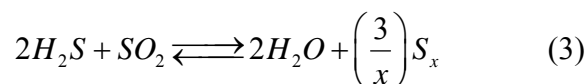
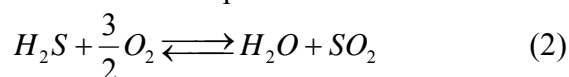
### 3. CLAUS SULFUR RECOVERY PROCESS

All Claus units involve an initial combustion step in a furnace. The combustion products then pass through a series of catalytic converters, each of which produces elemental sulfur.

The Claus process consists of the vapor-phase oxidation of hydrogen sulfide to form water and elemental sulfur, according to the overall reaction:



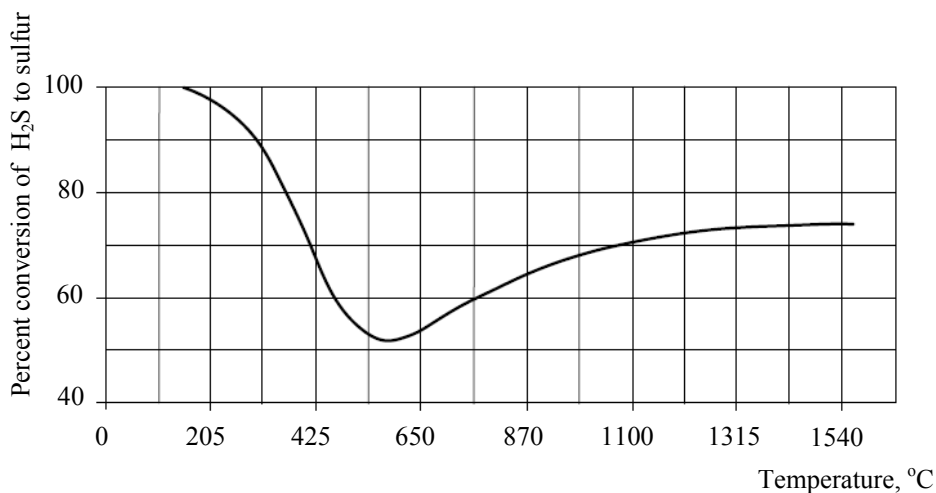
The above overall reaction does not represent the reaction mechanism or show intermediate steps. In practice, the reaction is carried out in two steps:



The first reaction is a highly exothermic combustion reaction, whereas the second is a more weakly exothermic reaction promoted by a catalyst to reach equilibrium.

Figure 2 shows the equilibrium conversion obtained for  $H_2S$  into elemental sulfur by the Claus reaction. Kohl and Nielsen (1997) state that the unusual shape of the equilibrium curve is caused by the existence of different sulfur species at different reaction temperatures.

They point out that at a sulfur partial



**Fig.2.** Equilibrium conversion of hydrogen sulfide to sulfur

pressure of 0.05 bar and temperatures below 370°C, the vapor is mostly S<sub>6</sub> and S<sub>8</sub>, but at the same partial pressure and temperatures over approximately 540°C, S<sub>2</sub> predominates. This shift in species causes the equilibrium constant in the reaction to shift from a downward slope to an upward slope, as shown in Figure 2. This behavior has a significant effect on the operation of the Claus process. The melting point of amorphous sulfur is 120°C, and its normal boiling point is 445°C. Figure 2 shows that the maximum conversion to sulfur by reaction (1) is obtained at temperatures near the melting point of sulfur, but to maintain sulfur in the vapor state, relatively high temperatures are required. Consequently, if the catalytic converters are to operate under conditions in which the sulfur does not condense on the catalyst, they cannot operate at optimum equilibrium conversion. This is the reason for having a series of converters, with the sulfur product withdrawn from the reacting mixture between converters. Withdrawing the sulfur product causes the reaction (3) to shift to the right, which results in more sulfur product.

Figure 3 and Figure 4 show simplified flow diagrams for the two common configurations, straight through and split flow, respectively. In the straight-through configuration, the first reaction takes place in a combustion furnace operating near ambient pressure (0.2 to 0.6 bar). The air flow rate is adjusted to react with one third of the H<sub>2</sub>S, along with any other combustibles, such as hydrocarbons and mercaptans. The H<sub>2</sub>S reaction is exothermic (24.000 kJ/m<sup>3</sup>, at 25°C at 1 atm) and is used to

produce steam in a waste-heat boiler. Both reactions take place in the furnace - boiler combination, and the gases exit the waste-heat boiler in the range of 260 to 343°C, which is above the sulfur dew point, so no sulfur condenses in the boiler.

The combustion furnace-boiler is followed by several catalytic reactors in which only the second reaction takes place because all the O<sub>2</sub> has been consumed in the furnace. Each catalytic reactor is followed by a condenser to remove the sulfur formed. The gas is cooled to 149 to 204°C in the condenser to remove elemental sulfur. The condenser generally achieves cooling by heat exchange with water to produce low-pressure steam. Vapor that leaves the condenser is at the sulfur dew point, so the gas is reheated before passing to the next converter to prevent sulfur deposition on the catalyst. A combustion-furnace flame temperature of 927°C should be maintained because the flame is not stable below this value. The straight-through configuration cannot be used at H<sub>2</sub>S concentrations below 55%, because the feed gas heating value is too low. Concentrations low as 40% are acceptable if the air or acid gas is preheated.

For H<sub>2</sub>S concentrations in the range 25 to 40%, the split flow configuration Fig.4. can be utilized. In this scheme, the feed is split, and one third or more of the feed goes to the furnace and the remainder joins the furnace exit gas before entering the first catalytic converter. When two thirds of the feed is bypassed, the combustion air is adjusted to oxidize all the H<sub>2</sub>S to SO<sub>2</sub>, and, consequently, the necessary flame

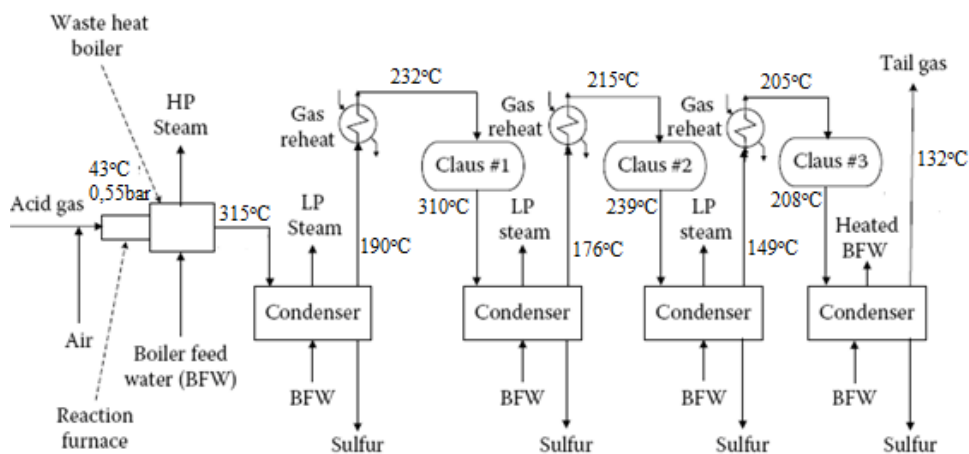
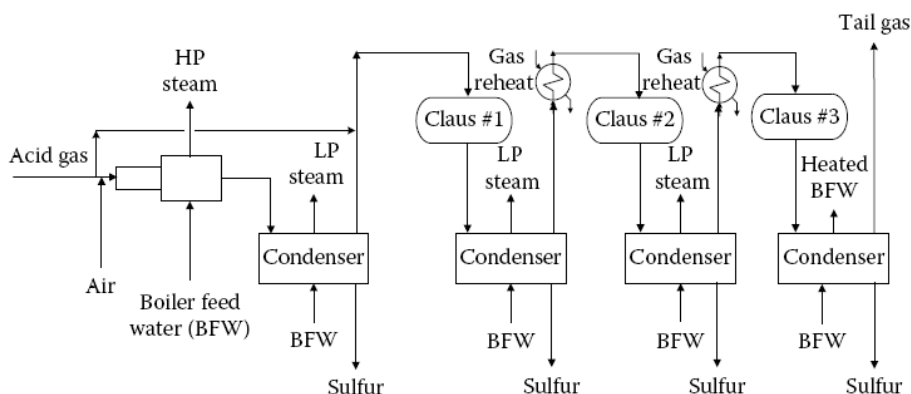


Fig.3. Straight-through Claus unit.



**Fig.4.** Split flow Claus unit. Typically two thirds of feed bypasses the reaction furnace.

temperature can be maintained.

The split-flow process has two constraints:

1. Sufficient gas must be bypassed so that the flame temperature is greater than approximately 927°C;

2. Maximum bypass is two thirds because one third of the H<sub>2</sub>S must be reacted to form SO<sub>2</sub>. If air preheating is used with the split-flow configuration, gases with as little as 7% H<sub>2</sub>S can be processed. Generally, the sulfur recovery in the conventional plants discussed above varies from 90 to 96% for two catalytic converters. It increases to 95 to 98% for three catalytic converters.

#### 4. CLAUS TAIL GAS CLEANUP

Until now, the off gas from the Claus unit was flared to convert the remaining H<sub>2</sub>S to SO<sub>2</sub>. Now, after sulfur emissions restrictions were imposed, environmental agencies demand higher sulfur recovery than can be achieved with a standard Claus unit, and additional treating of the Claus tail gas is needed. The tail gas cleanup entails either an add-on at the end of the Claus unit or a modification of the Claus unit itself.

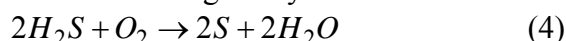
The processes for this final sulfur removal are generally divided into three categories:

- direct oxidation of H<sub>2</sub>S to sulfur;
- sub-dew point Claus processes;
- SO<sub>2</sub> reduction and recovery of H<sub>2</sub>S.

##### 4.1. Direct Oxidation of H<sub>2</sub>S to Sulfur

SUPERCLAUS is an example of selective oxidation for final sulfur removal. The process as described involves a slightly modified two-stage Claus unit followed by a third-stage catalytic reactor to oxidize the remaining H<sub>2</sub>S to elemental sulfur. Two reactors use the standard Claus catalyst, whereas the third reactor contains the selective oxidation catalyst. The Claus unit itself is operated with a deficiency of air so that the gas that exits the second reactor contains 0.8 to 3 vol% H<sub>2</sub>S. Sufficient air is added to this exit gas to keep the oxygen level in the 0.5 to 2 vol% range.

The mixture then goes to the third reactor, where the following catalytic reaction occurs:



The selective oxidation catalyst in the third reactor does not promote the reaction:



or the reverse reaction of sulfur with H<sub>2</sub>O:

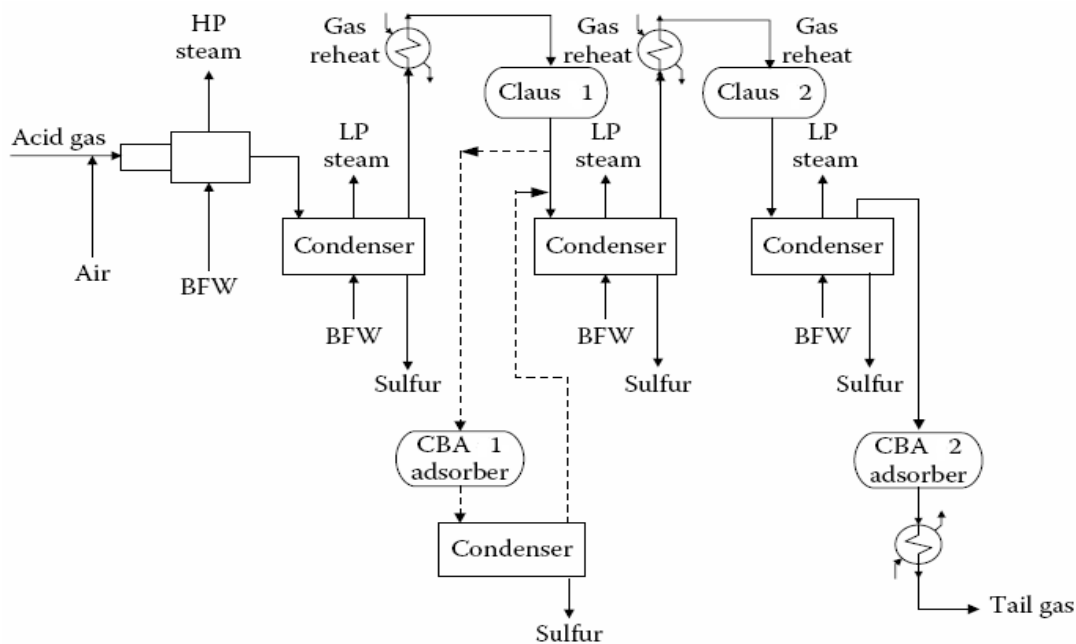


and, consequently, a total recovery rate of 99% or higher can be reached.

##### 4.2. Sub-Dew Point Claus Processes

From several processes of this category only the cold-bed adsorption (CBA) process is considered here because it is the most widely used. Figure.5 shows one of its many possible variations.

The front end of the unit is a Claus reactor, and the sub-dew point process takes place in the final two catalytic converters, CBA1 and CBA2.



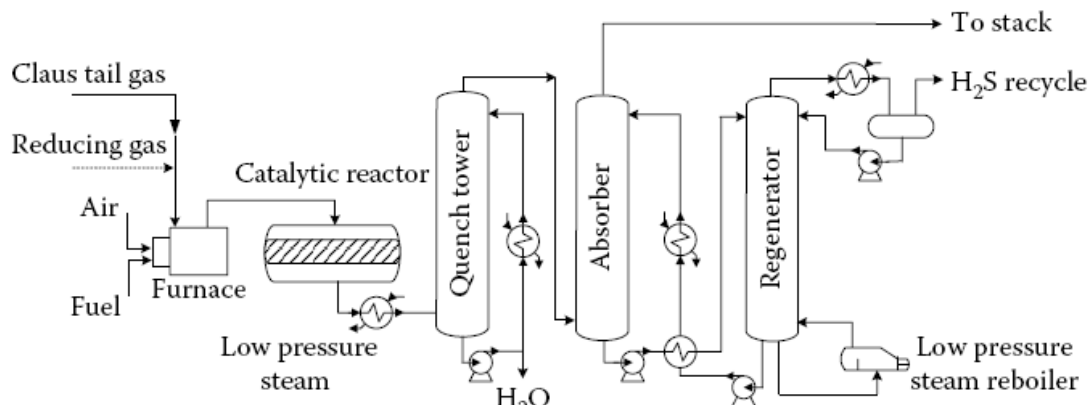
**Fig.5.** Cold-bed adsorption unit.  
(dashed line denotes regeneration stream)

After the gas leaves the final condenser, it is not reheated but is sent to the third converter (CBA2), which is operated at a temperature well below the sulfur dew point. This flow results in a better equilibrium conversion but deposits sulfur on the catalyst and causes a gradual loss of activity. During the period that CBA2 is in service, CBA1 is being heated and regenerated with a slip stream from Claus 1. After regeneration is complete, the reactor can be cooled with a slipstream from the final condenser. When the catalyst in CBA2 is exhausted, valves are switched, and CBA1 becomes the adsorbing reactor while CBA2 is regenerated. With CBA processes greater than 99% total sulfur recoveries can be obtained.

### 4.3. Reduction of SO<sub>2</sub> and Recovery of H<sub>2</sub>S

An example of the process that reduces the SO<sub>2</sub> in the Claus plant off gas back to H<sub>2</sub>S is the SCOT process. It uses amine treating to remove the H<sub>2</sub>S, which is recycled back to the Claus plant for conversion to elemental sulfur.

The process can produce an exit gas that contains 10 to 400 ppm of total sulfur, while increasing total sulfur recovery to 99.7% or higher. Figure 6 shows a simplified process flow diagram of the SCOT process. The feed, off gas from the Claus unit, is heated to 302°C in an inline burner, along with a reducing gas, H<sub>2</sub> or a CO and H<sub>2</sub> mixture. The reducing gas is supplied either from an outside source or generated by partial oxidation in an inline



**Fig.6.** Shell Claus Off gas Treating (SCOT) unit

burner. The mixture then flows to the SCOT catalytic reactor (cobalt-molybdenum on alumina), where the sulfur compounds, including SO<sub>2</sub>, CS<sub>2</sub>, and COS are reduced to H<sub>2</sub>S and water. The gas that leaves the reactor goes to a waste-heat exchanger, where it is cooled to about 160°C and produces low-pressure steam. The gas from the waste-heat exchanger then flows through a quench tower; where it is cooled to approximately 38°C by externally cooled recycle water in countercurrent flow. The water from the tower is condensed, and the excess water is sent to a sour water stripper. Gas from the quench tower then contacts an aqueous amine solution in the absorption column.

The amine is generally methyldiethanolamine (MDEA) or diisopropylamine (DIPA) to absorb H<sub>2</sub>S while slipping CO<sub>2</sub>. The gas that exits the top of the absorber contains very little H<sub>2</sub>S (10 to 400 ppm) and is sent to an incinerator. The rich amine that leaves the bottom of the absorber flows to the regenerator, where heat is applied to strip the H<sub>2</sub>S from the amine solution.

The overhead from the regenerator is cooled to condense the water, and the H<sub>2</sub>S is recycled to the Claus unit. Lean amine is cooled and returned to the absorber.

## 5. CONCLUSIONS

In order to meet SO<sub>x</sub> emission limits set by the Clean Air Act, refinery “sour gas” (also sometimes called “refinery gas,” “still gas,” “acid gas,” or “process off-gas” resulting from fractionation, cracking, coking, hydrotreating, and hydroprocessing) must be treated to remove sulfur, which can also be sold.

First, the hydrogen sulfide (H<sub>2</sub>S) is removed from the sour gas with a chemical solvent. Second, the gas is returned for use as fuel in refinery processes, and elemental sulfur is removed from the hydrogen sulfide using (primarily) the “Claus Process,” which utilizes heat and a catalyst. The sulfur recovery apparatus is commonly called the “Claus Unit,” “Sulfur Recovery Unit” (“SRU”), or “Sulfur Recovery Plant” (“SRP”). The gas from the SRU is referred to as “tail gas.”

The exit stream from Claus plants usually cannot meet environmental emission requirements, and, consequently, a tail gas cleanup unit (TGCU) is often employed to eliminate the last of the sulfur compounds. Some refineries use incinerators for treating such tail gas, others use the Shell Claus Offgas Treatment (“SCOT”) system, and still others use a solution tank treatment known as a Stretford process.

The most commonly used processes are Shell Claus off Gas Treating (SCOT), SUPERCLAUS, and cold-bed adsorption (CBA).

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