Design of Heat Recovery Equipments in Sulfur Recovery Unit

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Abstract

Recovery of elemental sulfur from refinery gases is an important problem both from environmental and economic points of view. The major source of recovered sulfur is hydrogen sulphide, mainly produced as a by-product in oil refineries as well as in natural gas processing plants. In sulfur recovery unit, elemental sulfur is produced via conventional or modified Claus process. Most Claus plants contain one non-catalytic conversion stage (the reactor furnace) followed by two or more catalytic conversion stages in series and can achieve 94-97% recovery of elemental sulfur. Important issues related to the design of the sulfur recovery process are discussed in this paper. The Claus reaction is highly exothermic, releasing a great amount of heat that can be recovered by generating steam in heat exchangers following the conversion stages. The hot combustion products from the furnace enter the waste heat boiler to generate high-pressure steam. Liquid sulfur is condensed in sulfur condensers while medium or low-pressure steam is generated. Unlike most of the shell and tube heat exchangers used in chemical process industry, design of heat recovery equipments in sulfur recovery units are unique. In this paper, special design features of these heat recovery equipments are discussed.

Keywords: Design features, heat recovery, sulfur condensers, waste heat boiler, Claus process.

Introduction

Recovery of elemental sulfur from refinery gases (i.e., acid gases from amine regenerator, sour water stripper, etc.) is an important problem both from environmental and economic points of view. The rise of sulfur volumes in waste gases together with tightening emission regulations leads to the increase of recovered sulfur production in sulfur recovery unit. Over 6.5 million tons of sulfur were recovered in 1989, representing about 63 percent of the total elemental sulfur market in the United States.

The major source of recovered sulfur is hydrogen sulphide, mainly produced as a by-product in oil refineries as well as in natural gas processing plants. Different processes are used worldwide for recovery of sulfur from hydrogen sulphide. In sulfur recovery unit, elemental sulfur is predominately produced via conventional or modified Claus process [1]. Claus process was developed and patented by Carl Friedrich Claus in 1882 [2]. Several modifications were developed on the process to increase the overall conversion of sulfur and produce a tail gas which satisfies the environmental regulations. The important commercially available modified processes include: the Amoco's Cold Bed Adsorption, the SNPA/Lurgi Sulfreen, the IFP, the SCOT, the Beavon, and the Wellman-Lord processes. Eow [3] presented a detailed review of different sulfur recovery technologies.

Most sulfur plants contain one non-catalytic conversion stage (the reactor furnace) and two or more catalytic conversion stages in series. The Claus reaction is highly exothermic, releasing a great deal of heat energy that can be recovered by generating steam in heat exchangers following the conversion stages. The hot combustion products from the furnace enter the waste heat boiler and are partially cooled, usually up to 350°C, by generating very high-pressure steam. The combustion products are passed through a series of condensers and catalytic reactors. Sulfur is condensed in sulfur condensers that are typically 3 to 5 in number. Medium or low-pressure steam is generated in sulfur condensers. Unlike most of the shell and tube heat exchangers used in chemical process industry, design of heat recovery equipments in sulfur recovery units are unique. In this paper, design features of these heat recovery equipments are discussed in details.

Claus Process

Schematic diagram of a conventional Claus process is shown in Figure 1. In the conventional Claus process, one-third of the acid gas (H_2S) is oxidized to sulfur dioxide in a reaction furnace using air. Remaining two-third of the acid gas reacts with the sulfur dioxide to produce elementary sulfur.

$$H_2S + 3/2\ O_2 \Rightarrow SO_2 + H_2O \qquad (1)$$
$$2\ H_2S + SO_2 \Leftrightarrow 3/n\ S_n + 2\ H_2O \qquad (2)$$

For refinery sulfur plants, the ammonia-bearing sour water stripper off-gas is routed to the acid gas burner mounted on the reactor furnace, along with most of the amine acid gas. The remainder of the amine acid gas is usually routed to side injection ports on the furnace so that the front zone of the furnace operates at a higher temperature to ensure good ammonia destruction. For gas-plant sulfur plants, there is normally only amine acid gas, which is usually all routed to the burner. Combustion air is routed to the burner, with the amount of air controlled to combust 1/3 of the H_2S to SO_2 via reaction (1). Sufficient air is also provided to combust the ammonia and hydrocarbons entering with the acid gas streams. The combustion products from the burner pass into the reactor furnace which provides sufficient residence time for all of the reactions to reach equilibrium. The furnace usually functions as a non-catalytic conversion stage, as the high temperature in the furnace will cause H_2S and SO_2 to combine via reaction (2) and form sulfur.

It is of utmost importance to maintain the required molar ratio of hydrogen sulfide and oxygen. This is achieved through two flow controllers acting on two parallel control valves, located on the discharge line of the air blower. One controller maintains the air to acid gas ratio and the other controller is reset by the signal coming from H_2S/SO_2 gas analyzer mounted on the tail gas line.

The Claus reaction is highly exothermic ($\Delta_r H^\circ_m = -108$ kJ/mol) and the thermodynamic equilibrium is favorably influenced by decreasing temperature. At the same time decreasing temperature reduces the rate of reaction. Therefore, the reaction has to be carried out catalytically. Due to the equilibrium limitation, this reaction has to be carried out in a multistage process with intermediate sulfur removal in order to achieve the H_2S conversions specified by environmental legislation. Processing under adiabatic conditions greatly increases temperature, which lowers equilibrium conversion to about 75%.

Effluent gas from the reaction furnace passes through a waste heat boiler to recover heat and to produce high-pressure steam. Effluent gas from the waste heat boiler is cooled in a condenser to condense sulfur. In order to avoid forming liquid sulfur in the downstream catalyst bed, condenser effluent gas is preheated and is sent to two or three catalytic reactors where Claus reactions occur at lower temperatures (below 325°C). The preheat exchanger heats the gas stream (to 225°C typically), often by using some of the high-pressure steam generated in the waste heat boiler. Heating oil or an electric heater may also be used. Sulfur is recovered after each catalytic stage by cooling converter effluent gas in a sulfur condenser. Usually, the catalysts, based on γ-Al_2O_3 or TiO_2, are applied in the process. The final effluent gas from the process is incinerated to SO_2 and vented to atmosphere.

The liquid sulfur from the condensers is passed through the sulfur locks and stored in an underground pit. Air is bubbled through the liquid pit to degas H_2S. Released H_2S is sent to the incinerator.

When the H_2S concentration in the acid gas is 50% or higher, the straight-through version of the Claus process (where all of the acid gas is routed to the acid gas burner) is generally used. Below this concentration, it is usually necessary to use the split-flow version of the process (where only a portion of the acid gas is combusted in the burner) in order to maintain a stable flame in the burner. Below an H_2S concentration of about 15%, a stable flame usually cannot be maintained in the burner, but special design techniques (such as supplemental fuel gas firing) can be employed to extend the range of the process to very lean acid gas streams.

The Claus process is generally limited to a sulfur recovery efficiency of 94-97%, depending on the H_2S concentration in the acid gas and the number of catalytic stages used. Although it is possible in some cases to achieve higher recoveries using additional catalytic stages, reaction equilibrium considerations generally limit the recoveries to these levels. For sulfur recoveries in the intermediate range of 97.5-99.5%, the cold bed adsorption process is usually a better choice. For recoveries in excess of 99.5%, the modified Claus process with tail gas cleanup is normally used.

In conventional as well as most of the commercially available modified Claus processes, the unit is capable of operating at a turndown from

15% to 100% of design capacity without any mechanical modification of the equipments.

Heat Recovery Equipments

Waste heat boiler and sulfur condensers are the main heat recovery equipments of sulfur recovery unit. Design features of these equipments are discussed in details.

Waste Heat Boiler

Waste heat boiler is installed just after the reactor furnace. High-pressure steam (usually up to 45 kg/cm^2-g) is generated by cooling the combusted gas from about 1350°C to around 350°C. Waste heat boiler is a fire tube boiler with steam generation on the shell side. This design helps protect the tube sheet and tubes through proper circulation. Waste boilers are usually of kettle type design with included steam generation in the submerged tubes. Whenever the pressure of the generated steam exceeds 45 kg/cm^2(g), a separate steam drum with natural circulation is provided.

Ferrules (ceramic inserts) are used at the inlet tube sheet to transfer heat flux away from the tube sheet into the region where boiling occurs, thus keeping the tube inlet and tube sheet region cool. Heat flux at tube inlet of waste heat boiler is limited to 80 kW/m^2.

A two-gas pass boiler may be used, though single pass designs are preferred. Provision for sulfur recovery is made at the gas exit zone by using sulfur drains, which are kept warm by circulating steam. Since the gas pressure is atmospheric, casing designs are not special as in reformed gas boiler in hydrogen plants. Adequate refractory is used ensuring the casing is hot and is near or above the sulfur dew point. Gas bypass systems are not generally used. Carbon steel tubes are adequate. Economizers are not recommended due to low temperature corrosion concerns. Steam outlet nozzles are provided with demister. Additionally, an electric heater is employed for steady operation of the unit at turndown (i.e., 15% to 35%). Square tube pitch is preferred in waste tube boilers.

External insulations are applied on the shell side and outlet channel side. However, external insulations are not preferred on inlet channel.

Note that, some H_2S (2-4%) is remade in the waste heat boiler from sulfur reacting with H^+ (dissociated hydrogen).

Sulfur Condensers

Schematic diagram of a sulfur condenser is shown in Figure 2. The sulfur bearing gases from the Claus reaction is cooled down below the dew-point of sulfur in sulfur condensers to condensate the elemental sulfur. Melting and boiling points of elemental sulfur are 119°C and 444.6°C, respectively. Ideal condenser temperature is about 10°C above the sulfur dew-point. Sulfur condensers are conventional shell-and-tube heat exchangers (usually kettle type) with few special design features. Medium or low-pressure steam is generated in the shell side of sulfur condensers.

The liquid sulfur outlet nozzles should be steam jacketed to prevent cooling down of liquid sulfur. It also increases the flowability of liquid sulfur.

Tubes of the sulfur condensers are typically sloped (1-3 degree) towards outlet. The sulfur condenser vessel is equipped with a disengagement section (demister) on the steam outlet nozzles in order to allow for efficient separation of the liquid sulfur from the process gas. A collection vessel equipped with continuous level control is used to store and remove the product sulfur from the process.

The second stage of heat recovery takes the form of sulfur condenser; it is a low pressure steam generating section, where multiple low temperature gas streams leaving the various stages of catalytic conversion ranging from 180-260°C are cooled in the condenser generating 1-5.5 kg/cm^2(g) saturated steam. The first and the second condensers produce steam at 3-5.5 kg/cm^2(g) and 1-1.5 kg/cm^2(g) steam is produced in other condensers. Here too the drains have to be kept warm to prevent solidification of sulfur. Carbon steel tubes are adequate. Steam jacketed filters are provided at the outlet of sulfur condensers to avoid dust carry-over in sulfur run-down lines.

For sulfur recovery units of 50 ton/day or smaller capacity (depending on the feed gas composition), usually 2 to 3 condensers are combined in a single shell to optimize the design (see Figure 3). Single shell, fire tube boilers are widely used for this application if the gas flow is small, as they are less expensive than elevated drum designs. Separate exchangers may be used for each stage of conversion if the gas flow is large.

Inlet and outlet channels are applied with a layer of castable at the bottom to prevent formation of any pocket for accumulation of liquid sulfur. Steaming out requirement is not applicable to sulfur condensers to prevent refractory damage. External insulation (mineral wool) are applied on the shell side, outlet and inlet channel sides.

COS and CS_2 formed in the Claus reactor must be converted to CO_2 and sulfur. This is a slow reaction and requires substantial residence time. This is typically achieved by holding the second condenser at a high temperature. In this process, 10% of incoming sulfur can be lost if adequate time is not allowed.

Sulfurcrete consists of elemental sulfur, salts formed from sulfur plus CO_2, SO_2, NH_3 and dust from abrasion of Claus catalysts. The hardness of this material matches that of granite. Over time sulfurcrete builds up and plugs the tubes of sulfur condensers. Traces of sulfuric acid are formed under the sulfurcrete layer leading to corrosion. For these reasons sulfurcrete has to be removed. Dry ice blasting is proposed to be the best way of removing sulfurcrete [4].

Conclusions

More than 2.6 ton of steam is generated per ton of sulfur produced. This has a direct effect on the energy efficiency of the entire plant. Steam produced is linked with the power production of the plant. Optimization of the steam produced at different levels become important, eventually making the design of the heat recovery equipments play an important role in the overall energy efficiency of the plant.

Design of waste heat boilers and sulfur condensers is more of an art than science. These equipments are designed based on experience as they involve several special features. In this paper, an attempt has been made to bring some of these unique design features to open literature.

References

[1] R.N. Maddox, Gas Conditioning and Processing, Campbell Petroleum Series, vol. 4, Norman, Oklahoma, 1982.
[2] H. Fisher, Hydrocarbon Processing (1974) 27.
[3] J.S. Eow, Environmental Progress 21 (2002) 143.
[4] M. Heisel, A. Buinger, Sulphur 274 (2001) 43.

Declaration

All views expressed in this article are those of the authors and do not necessarily represent the views of their respective employers.

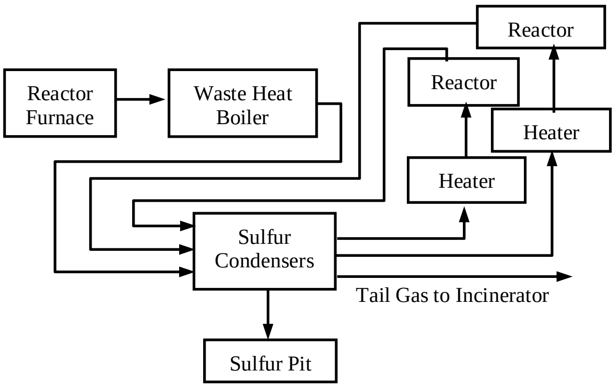

Figure 1. Schematic diagram of a conventional Claus process.

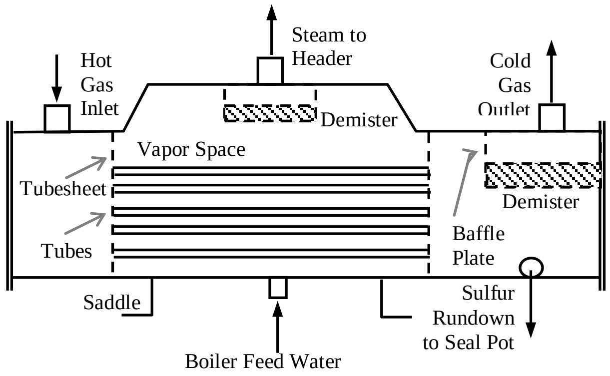

Figure 2. Schematic diagram of a sulfur condenser.

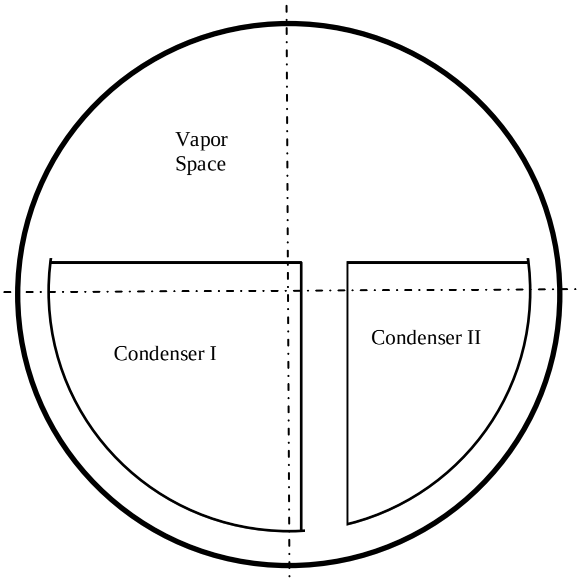

Figure 3. Cross sectional view of a sulfur condenser showing multiple condensers integrated in a single shell.