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The effective parameters at choosing an appropriate tail gas treatment process

Hamid Reza Mahdipoor*, Hajar Yousefian, Hamed Naderi, Majid Kakavand

Department of Process and Equipment Technology Development, Research Institute of Petroleum Industry, West Bld. of Azadi Stadium, Tehran, (IRAN)

E-mail: mahdipoor@gmail.com

ABSTRACT

In order to produce sulfur and also prevent environmental pollution, output acid gases from oil and gas refineries are converted to sulfur in sulfur recovery units (SRUs). The conversion of these pollutant gases to sulfur hardly exceeds 97% which leads to excessive sulfur dioxide sent to the flare and hence high pollution around refineries. Thus, with the current strict environmental regulations, it is necessary to somehow improve the performance of SRU. Tail gas treatment units can achieve overall efficiencies of more than 99% by eliminating a certain portion of the acid gases which are present in the tail gas of sulfur recovery units. In this paper, the technology of tail gas treatment will be investigated. Furthermore, the role of applying this unit in reduction of environmental pollutants is illustrated.

KEYWORDS

Sulfur recovery;
Tail gas treatment;
Environmental pollution.

INTRODUCTION

Claus process is widely used for conversion of hydrogen sulfide to elemental sulfide[1]. This process is used to produce elemental sulfide from byproducts of gas sweetening processes in refineries, chemical plants and gas processing units[2]. Claus process consists of a reaction furnace, a waste heat boiler (WHB) and a series of catalytic converters & condensers Figure 1. In literature lots of reactions have been identified to take place in reaction furnace[3-6]. The overall reaction of the Claus process is as following:

$$2H_2S + O_2 \Rightarrow S_2 + 2H_2O \quad (1)$$

In first stage, one third of the inlet hydrogen sulfide to the reaction furnace oxidizes to SO_2. The main oxidization reaction is as follows:

$$H_2S + \frac{3}{2}O_2 \Rightarrow SO_2 + H_2O \quad (2)$$

About 60% of the SO_2 resulted from reaction (2) reacts with H_2S and is then converted to elemental sulfur.

$$2H_2S + SO_2 \Leftrightarrow \frac{3}{2}S_2 + 2H_2O \quad (3)$$

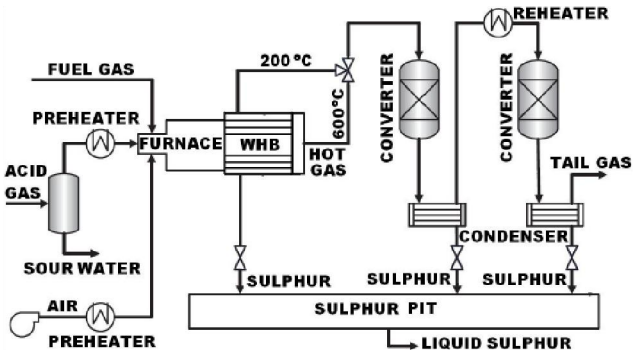

Figure 1 : The schematic diagram of a typical Claus process

Waste heat boiler (WHB) which is located after reaction furnace recovers heat by cooling the gas products[6,7] and separates the produced sulfur in the fur-

nace from the gas phase after condensation. In second stage which is catalytic, the un-reacted SO_2 and H_2S react in a fixed bed reactor in vicinity of Alumina catalyst according to relation (3) and are converted to water and elemental sulfur[6-8]. Achievement of high conversion rate for the above exothermic reaction requires operation at low temperature which leads to low reaction rate and so it will be necessary to use catalyst. Even with these conditions, to yield high efficiency, it will be essential to have a multi-stage reaction with intermediate cooling and condensation[8].

To achieve the maximum conversion rate in catalytic reactors, the produced sulfur in different stages of Claus process is liquefied and then recovered. The unrecovered sulfur either elemental or in compositions like H_2S, COS or CS_2 is burned in tail gas incinerator, converted to SO_2 and sent to atmosphere[7].

To increase the total recovery of sulfur and decrease the environmental pollutants, tail gas treatment unit is incorporated before incinerator[7]. In this unit, the output gas from Claus will be processed to recover as much of its sulfur content as possible. There are lots of processes used for treatment of tail gas such as absorption processes with amine solvent (e.g. SCOT process under Shell license), dry subdewpoint processes (e.g. Sulfreen process under Lurgi license), wet subdewpoint processes (e.g. Clauspol process under IFP license) and Liquid Redux processes (e.g. Sulfiran process developed in Iranian Research Institute of Petroleum Industry). Among these processes, the first and second ones are more common and have been industrialized in more places[9].

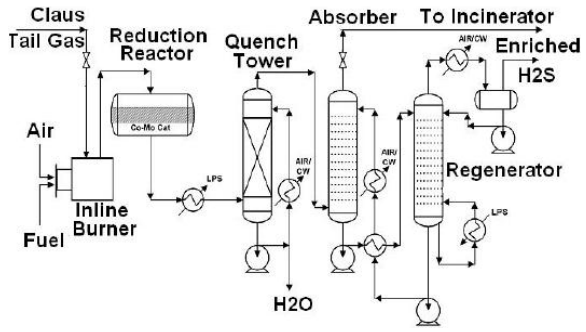

Figure 2 : Schematic diagram of a typical SCOT process

In absorption processes with amine solvent, the outlet sulfur compositions of Claus unit are converted to H_2S in hydrogenation reactor, absorbed in the amine contactor (amine absorber column) and then stripped in the amine regenerator (stripper column). The stream enriched with H_2S is then returned to the beginning of the Claus unit and is converted to sulfur. Figure 2 illustrates the schematic diagram of absorption processes with amine solvent[10,11].

Sulfreen is one of the most important models of dry subdewpoint processes. This process was first introduced by Lurgi and SNPA companies in 1968. The first industrial unit of this process with a feed capacity of 1000 tons per day was developed in 1970. Nowadays more than 50 industrial units of this process with different capacities up to 2200 tons per day are working all around the world. The catalyst used in this process was originally Activated carbon which was gradually replaced by Activated alumina. In this process the existing SO_2 and H_2S in the tail gas are converted to elemental sulfur in subdewpoint temperature and catalytic beds. Activated alumina plays the role of both catalyst and adsorption agent. Alumina has a high sulfur adsorption capacity and easy sulfur desorption capability which has made it the best choice for this process. Adsorption and recovery is alternatively achieved in two Sulfreen reactors. Switching time from one bed to another is adjusted according to the catalyst adsorption time capacity. After completer absorption of sulfur by catalyst in absorption bed, it will change its role for desorbing bed in which neutral hot gas entered by blower will cause the adsorbed sulfur to evaporate and leave the reactor for condensation step. After completion of desorption process, bed temperature is decreased making it ready for another absorption process. Alternative absorbing and desorbing in beds has caused Sulfreen to be identified as a semi-continuous cyclic process. The most important probable problem of this process is maintenance of desorption process blower and gas bed exchange valves which are eliminating by selecting suitable materials for them. Depending on the existing SO_2 and H_2S in the tail gas, it will be possible to reach a recovery of 99% by Sulfreen process as addressed in literature. Figure 3 illustrates a schematic diagram of the Sulfreen process[12].

In wet subdewpoint processes such as Clauspol[13]. The outlet gas of the Claus process (i.e. tail gas) is directly converted to sulfur in a catalytic reactor. In this method, tail gas comes to a counter-current contact with catalyst/solvent in a catalytic column. SO_2 and H_2S

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are absorbed by liquid phase and in vicinity of catalyst. Elemental Sulfur is formed according to reaction 3 and exited from the bottom of the column. Sulfur free catalyst and solutions are then recycled to the top of the column. In this process, by injection of steam, the column is kept stable at a temperature higher than solidification one to increase the efficiency. In literature the efficiency of this approach has been addressed to be more that 99.3%[14]. The schematic diagram of Clauspol process has been depicted in Figure 4.

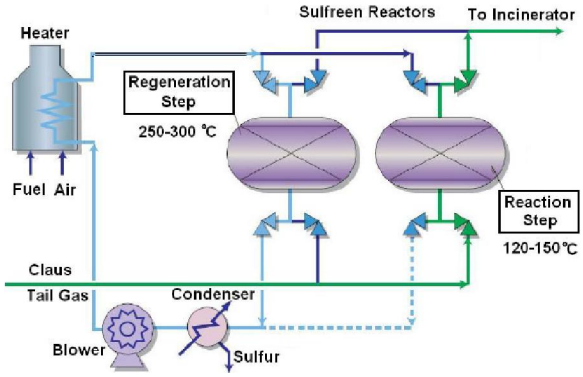

Figure 3 : Sulfreen process schematic diagram

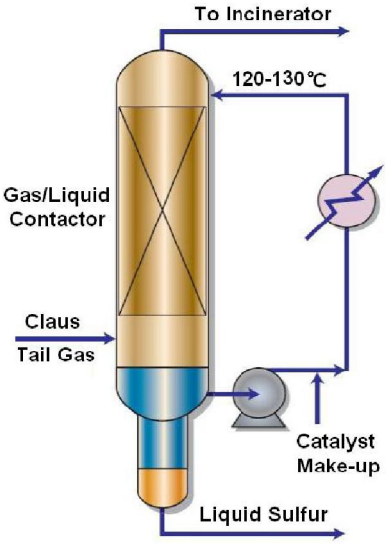

Figure 4 : IFP Caluspol process schematic diagram

Liquid Redux processes provide direct oxidation of H_2S to elemental sulfur in ambient temperature with conversion rates of nearly 100%. These processes are highly flexible and may be applied for various feeds with different amounts of H_2S. High expenses for chemical materials, lower produced sulfur quality (lower purity of produced sulfur in compare to Claus process) and in some cases failure to treat high pressure gases are some disadvantages of Liquid Redux processes[15]. Sulfiran process developed and localized in Iranian Research Institute of Petroleum Industry is based on selective elimination of hydrogen sulfide from the gas mixture which will be in turn converted to elemental sulfur. In this process, catalyst solution of iron chelate in contact with the tail gas, will directly convert the hydrogen sulfide to elemental sulfur according to the following reaction:

$$2Fe^{3+}(aq) + H_2S \rightarrow 2H^+ + S^\circ + 2Fe^{2+}(aq) \quad (4)$$

Iron chelate catalyst shall be manufactured in a manner to be resistant against various pressure ranges and different site conditions. It shall be also stable at operating conditions and shall not result any byproducts. In general, this method is more economical than amine process for treatment of low volume gases. The expense of this process when used for elimination of sulfur from high volume of gases with low sulfur content (less than 15 tons per day) is relatively low. This process may be also applied for elimination of hydrogen sulfide and production of gases enriched with carbon dioxide in cases where carbon dioxide to hydrogen sulfide ratio is high[16]. Figure 5 depicts schematic diagram of a typical Liquid Redux process[17].

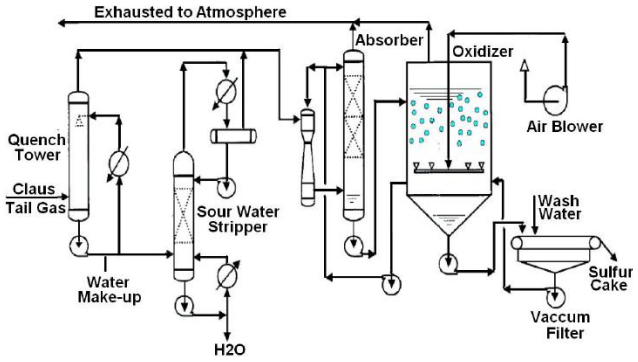

Figure 5 : Schematic diagram of tail gas treatment using liquid redux process

Regarding to the mentioned contents, the amine process seems to be more appropriate than the other processes. Researches and industrial experiences show that amine process has the highest efficiency among the existing processes for wide range of gas flow rates and can increase the conversion rate to an amount more than 99.6%. In addition, this process completely eliminates the environmental problems resulted from exhaustion of H_2S into atmosphere. In this paper, the results of a typical amine based TGT unit are presented and com-

pare with the recovery of a traditional Claus unit without tail gas treatment.

SIMULATION OF A TYPICAL INDUSTRIAL TAIL GAS TREATMENT (TGT) UNIT

In this section a typical SCOT tail gas treatment unit will be investigated. SCOT process was first developed by Shell to improve the efficiency of sulfur recovery unit in SRU. As illustrated in Figure 2, outlet tail gas stream from Claus unit enters the reduction reactor in which all its sulfur compositions including COS, CS_2 and SO_2 are converted to H_2S. After cooling the gas, this stream enters the amine absorption column. H_2S enriched stream (rich amine) goes towards the regeneration column from the bottom of absorption column. Lean amine stream from the bottom of the stripper is recycled to absorption column and the stream with high content of H_2S from the top of the column is returned to the input of the SRU ad mixed with Claus feed. The stream exiting from the top of the absorber (the off gas of SCOT process) which includes a negligible amount of H_2S is directed to incinerator where is burned with fuel gas. By incorporation of SCOT process in SRU, approximately all of the input sulfur compounds will be converted to elemental sulfur and the environmental pollutants will be minimal[9]. To investigate the role of Tail Gas Treatment unit in reduction of environmental pollutants, a common refinery Claus unit was studied. Sulfur recovery units have usually two types of feeds, acid gas and sour gas coming from amine sweetening and sour water treatment units, respectively. The specifications of the input acid gas and sour gas to this unit are given in TABLE 1 and TABLE 2, respectively.

TABLE 1 : Specifications of the input acid gas to Claus unit

Property	Value
Temperature	41 ℃
Pressure	1.8 bara
Molar Flow	55.84 Kmole/h
Composition (mole %)	
H_2S	97.9
C2H6	0.35
H2O	1.75
NH3	0

The results achieved from the simulation of the Claus unit without TGT, show a sulfur recovery amount of 42.29 tons/day. In this case, the total sulfur recovery for this SRU unit will be 97.28%. The specifications of the output tail gas of this unit have been presented in TABLE 3. This gas from the Claus unit is directed to incinerator where is burning with fuel gas and then sent to the atmosphere. The results show the output gas from the incinerator flare contains more than 1700 ppm of SO_2 gas which is not acceptable from environmental point of view.

TABLE 2 : Specifications of the input sour gas to Claus unit

Property	Value
Temperature	90 ℃
Pressure	1.8 bara
Molar Flow	3.22 Kmole/h
Composition (mole %)	
H2S	56.53
CO2	0.03
H2O	21.79
NH3	21.65

TABLE 3 : Specifications of the Claus output tail gas

Property	Value
Temperature	130 ℃
Pressure	1.32 bara
Molar Flow	176 Kmole/h
Composition (mole %)	
H2S	0.55
SO2	0.28
H2	1.77
H2O	37.39
N2	59.79
CO	0.03
CO2	0.19

At the next step, a SCOT TGT Unit was incorporated for treatment of Claus Unit output tail gases. Simulation results showed that conversion rate increased to 99.93% and the sulfur production reached 43.44 tons/day. TABLE 4 shows the specifications of the TGT off gas which is directed to incinerator. As shown in this table, the amounts of SO_2 and H_2S are drastically decreased. Also the results show that the amount of SO_2 in the incinerator flare gas which is exhausted to atmosphere has decreased to 127 ppm when using TGT unit. This amount of SO_2 doesn't violate the environmental regulations and avoids pollution problems resulted from SO_2 emission in atmosphere.

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TABLE 4 : Specifications of the TGT off gas

Property	Value
Temperature	40.1 ℃
Pressure	1.07 bara
Molar Flow	135 Kmole/h
Composition (mole %)	
H2S	0.01
SO2	0
CO2	1.9
N2	88.65
H2	2.9
H2O	6.53

CONCLUSIONS

To avoid environmental pollution, output acid gases from oil and gas refineries are converted to sulfur in sulfur recovery units. The conversion rate of these pollutant gases to sulfur hardly exceeds 97% which is in contrast with the current strict environmental regulations and so it is necessary to increase the efficiency of these units. Tail Gas Treatment Units provide conversion rates of more than 99% by eliminating a high amount of sulfur recovery unit residual output acid gases. In this paper tail gas treatment technology was investigated and it was concluded that SCOT process was the most suitable option. Then a typical Claus unit was studied and compared with the performance of a Claus unit equipped with a SCOT TGT section. The results showed that TGT units play an important role in reduction of environmental pollutants.

REFERENCES

[1] B.Zare Nezhad; An investigation on the most important influencing parameters regarding the selection of the proper catalysts for Claus SRU converters, J.Ind.Eng.Chem., **15**, 143-147 **(2009)**.

[2] S.Signor, F.Manenti, M.G.Grottoli, P.Fabbri, S.Pierucci; Sulfur recovery units: Adaptive simulation and model validation on an industrial plant, Ind.Eng.Chem.Res., **49**, 5714-5724 **(2010)**.

[3] K.A.Hawboldt, W.D.Monnery, W.Y.Svrcek; New experimental data and kinetic rate expression for H2S cracking and Re-Association. Chem.Eng.Sci., **55**, 957-966 **(1999)**.

[4] W.D.Monnery, K.A.Hawboldt, A.E.Pollock, W.Y.Svrcek; Ammonia pyrolysis and oxidation in the Claus furnace, Ind.Eng.Chem.Res., **40**, 144-151 **(2001)**.

[5] P.D.Clark, N.I.Dowling, M.Huang; Chemistry of the Claus front-end reaction furnace. Hydrocarbon reactions and the formation and destruction of CS_2. Proceedings of the Brimstone Sulfur Recovery Symposium, Vail, CO, Sept. 23-26, **(1997)**.

[6] H.R.Mahdipoor, K.Khorsand, R.Hayati, H.Javaherizadeh; Adjusting critical parameters for designing the sulfur recovery units (SRUs), Chemical Technology, an Indian Journal, **7**, **(2012)**.

[7] L.V.Nasato, K.Karan, A.K.Mehrotra, L.A.Behie; Modeling reaction quench times in the waste heat boiler of a Claus plant, Ind.Eng.Chem.Res., **33**, 7-13 **(1994)**.

[8] M.P.Elsner, M.Menge, C.Müller, D.W.Agar; The Claus process: Teaching an old dog new tricks, Catalysis Today, **79**, 487-494 **(2003)**.

[9] Anonymous; Gas processors suppliers association (GPSA). Engineering Data Book; GPSA Tulsa, Chapter, 22 **(1987)**.

[10] Nadhir, A.Al-Baghli, Steven A.Pruess, Victor F.Yesavage, M.Sami Selim; A rate-based model for the design of gas absorbers for the removal of CO2 and H2S using aqueous solutions of MEA and DEA, Fluid Phase Equilibria, **185**, 31-43 **(2001)**.

[11] K.Van den Brand; Shell's low cost SCOT process, Sulphur Recovery Symposium, Vail, **(2002)**.

[12] W.Willing, T.Lindner; Lurgi's TGT processes and new operational results from Sulfreen plants, Presented at the SULPHUR'94 Conference, Tampa, Florida, Nov. 6-9, **(1994)**.

[13] C.Barrère-Tricca, J.P.Margotin, D.H.Smith; Thirty years of operating experience with the clauspol process, Oil & Gas Science and Technology–Rev.IFP, Éditions Technip, **56(2)**, 199-206 **(2001)**.

[14] G.Goar, J.Sames; Tail gas clean up processes, 33th gas conditioning conference, Norman, Oklahoma, March, **(1983)**.

[15] P.Y.Le Strat; New redox process successful in high pressure gas stream, Oil & Gas Journal, November, **26**, 46-53 **(2001)**.

[16] Khaled Forsat, M.Saadi, M.Hosseini Jenab, J.Sadeghzadeh Ahari; Experimental investigation and modeling of hydrogen sulfide absorption column in sulfiran process, Iranian Oil Research Journal, **62**, 44-52 **(2010)**.

[17] G.Nagl; Emerging markets for liquid redox sulphur. SULPHUR '97 Conference, Vienna, Austria, **(1997)**.