Buletin Teknol. Tanaman, Bil.12, Tambahan.2 (2015): 387-392

Simulation and Optimization of Energy Consumption of Sulfur Recovery Unit at Fifth Refinery of South Pars Gas Complex

Gholam Hossein Gholami, Mohammad Sharifi

Abstract
Increasing demand of industry to sulfur with respect to environmental laws has led to the removal of pollutants, to give more attention to sulfur recovery unit at oil, gas and petrochemical so that we can maximize the efficiency of these units. In this article we have tried to evaluate the processes related to the sulfur recovery unit sweetening of sour gas from a gas refinery, in the meantime main process is the reaction Claus and detailed expression. The reaction furnace is located in the heart of the recovery of the class has been studied and modeled in order to obtain the temperature and rate of reaction. Then, with the ASPEN HYSYS process simulation software has been paid to energy efficiency made possible by it. To use this simulator should be considered early series of simplifying assumptions, because the information is not available fully Claus reaction kinetics. After process simulation using MATLAB software bundle is provided with the capability, through which energy optimization can be evaluated and the other used for heating and cooling and saving the energy.
Key words: sulfur recovery unit, Claus reaction, Reaction furnace, ASPEN HYSYS, Energy optimization

Introduction

Gas resulting of oil and gas resources and petrochemicals, including the amounts of CO_2 and H_2S is called sour gas. H_2S is a highly toxic substance that should be removed, this gas is also highly corrosive when burning producing SO_2 which is toxic and corrosive [1] so, converting H_2S to sulfur and sulfur recovery process is very important in a sour gas, because a toxic and corrosive material is converted into a marketable and valuable works (Sulfur). Sulfur specifications are as below. One of the processes in the refining industry is the process of recovering sulfur from acid gas flowing. In worldwide, huge efforts have been done to increase the efficiency of this process and to reduce investment costs.Simulation software help process engineers, because using the software engineer can introduces all effect parameters in certain circumstances to investigate the area on outflows and by measuring the amount of outflows of optimal configuration for process. In this paper, using ASPEN, HYSYS software or using programming languages, simulation can be done. In this article the physical specifications and product application process (sulfur) will be discussed. Then a variety of sulfur recovery processes is performed, the latest and newest technologies in order to develop and optimize sulfur recovery process in the world have been proposed.A conclusion is the fact that the basis of all development and changes is the Claus old method. Therefore, the following principles are detailed and precise expression of the Claus process. Due to the material it is clear that the most important stage of the Claus process is stage combustion or reaction furnace. Due to the lack of kinetics, reaction and time species radical action, macroscopic modeling furnace is done. Then, using software of ASPEN HYSYS process simulation in static mode and the results of the simulation were compared with actual results and optimizing energy consumption in these units is done.

Properties and Application of Sulfur:

Sulfur is a non-metallic chemical element with the chemical symbol is S. sulfur is achieved coal, oil and natural gas. The apparent profile is fragility of this element, yellow, odorless, tasteless and non-soluble in water. Two forms has crystalline and is made sulfur atoms and molecules octagonal. The viscosity of sulfur liquid increases with increasing temperature and temperature and this effect creates long polymer chains of sulfur molecules. [5] Figure 1-1 shows how the viscosity of liquid sulfur H_2S is solved. When the temperature rises above C ° 160, liquid sulfur dye is dark. At temperatures 250° C reaches to dark brown / black and at boiling point of 444° C will be dark.

Figure 1-2 shows the distribution of sulfur components S_2, S_6 and S_8. Sulfur is an activated chemical element and generates many compounds and also participates in the organic compounds such as mercaptans and thiols. Sulfur in the air burns with a blue flame and forms the SO_2. [6]

Figure 1. Effect of hydrogen sulfide on the viscosity of the sulfur molten liquid and its relation with temperature

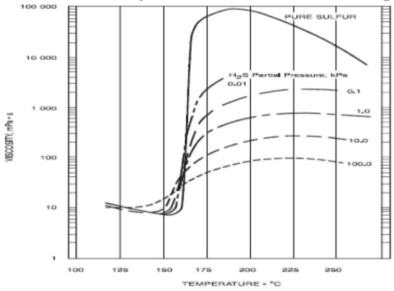
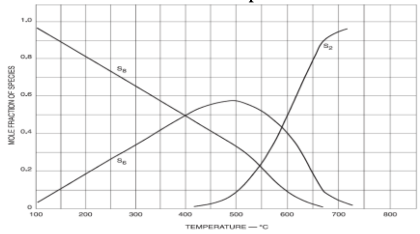


Figure 2. the distribution of sulfur vapor based on the temperature



Methods to remove the H_2S of sour gas

So far, several processes are used to remove H_2S from the sour gas.

Multiple processes include the following:
1) Adsorption on solids
2) Direct conversion
3) Attract reversible

Adsorption on solids

From a carbon or molecular sieve adsorbents are used. H_2S is removed by steam or hot gas from the acid gas under vacuum, that this method is a physical state.

Direct Conversion

In this method, hydrogen sulfide in the sour gas by a homogeneous aqueous solution engages in chemical reaction and is directly converted to sulfur. The resulting solution is restoring to its original state and its sulfur content is separated in different ways. This method is used for of low-pressure and low concentrations of H_2S .

Reversible absorption

This method is superior to other methods. In this method, a solvent used in the H_2S selectively absorbs the acid gas. This method is reversible chemical reaction between H2S and a weak alkaline solution and low salt is broken by heating to raw material. [3] Alkanolamines RNH_2 formula is category of organic derivatives of ammonia with good alkali and organic solvent. The most common amino acid that has been used is mono-ethanol amine or MEA, which is the strongest Alkali and easy combined with H_2S and CO_2 selectively. Choose MEA is due to two things: First, the lowest molecular weight and the second weight and volume have the highest potential separation. In addition, they are chemically stable and easily placed under the disposal of steam. [9]

Claus method

Although the Claus reaction was identified in 1883, but the production of sulfur in this way was not cost-effective in a single unit. From mid-twentieth century due to growing demand from various industries to sulfur, sulfur recovery unit operation began growing. Generally, a third of the hydrogen sulfide is burned in furnaces and air SO_2 is produced. The produced SO_2 is engaged with the remainder of the H_2S in Claus reaction. [7] This method has several stages that ultimately is catalyst and heat and molten sulfur is prepared and stored. But since that yield is 98-95 percent, it is essential that environmental pollution control devices that use a lot of expenses.

In the Claus process, below reactions are used to converting hydrogen sulfide to sulfur.

$$H_2O \quad + \quad SO_2 \qquad {}^{3}\!/_{2}\, O_2 \rightarrow + H_2S$$

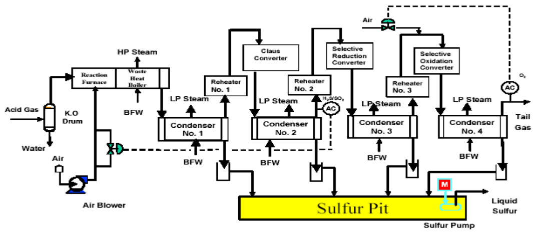
$$H_2O \quad + {}^{3}\!/_{2}\, S_2 \qquad SO_2 \rightarrow \quad + \quad 2H_2S$$

Most of sulfur plans include a non-catalytic converter (reaction furnace) and there are two or more catalytic stages. Claus is an exothermic reaction and release large amount of heat that the heat can be used for steam production in converters. [4]

Details of the overall process

For remediation of sulfur, sour gas with water repellence, along with a portion of the amino acid to take place gas combustion. Other amino acid gas also goes directly to the furnace. (Along with a controlled amount of air for combustion, one third of hydrogen sulfide and sulfur dioxide by reacting 3) The combustion products move to reaction furnace from burning where acid gas to raise the temperature and bring the temperature of the combustion temperature, mixed with the acid gas. Furnace acts as a non-catalytic stage. High temperature furnace causes H_2S and SO_2 accordance with the reaction (4). [6]Hot products of combustion in the boiler is cooled to the temperature of step K°700 - 585, as a result, the steam pressure kPa (ga) 4122 or higher is produced. Combustion products at K °463- 444 again to cool in condenser sulfur to produce medium pressure steam. (KPa (ga) 446.56-274.82) In this field, gas is so cool that part of the liquid sulfur, liquid sulfur formed is separated from the gas and collected in the containers. Flow of output of the first sulfur condenser into the catalytic bed reactor, but to avoid the formation of liquid sulfur in the lower part of the flow of catalyst bed is heated exhaust gas condenser and then into the catalyst bed. These converters warm the gas stream to a temperature in K °505- 488. This heat is supplied from the high-pressure steam or electric heaters. [8]Heated flow enter into the first catalytic reactor including deep bed "48" 36 of the catalyst particles. More conversion of sulfur to the aluminum catalyst is occurred. Specifically, 70 percent of H_2S and SO_2 is reacted over the top reaction to form sulfur. Exhaust gas from the reactor (at K°616-560) in the second sulfur condenser is cooled the vapor with pressure and temperature average K°449- 433 is produced. Liquid sulfur, respective sulfur separated and collected in containers. This process usually followed by one or two stage of catalytic thermal reaction and condensation. Sulfur is removed of last condenser with temperature between K°421- 394. This temperature depends on the vapor pressure in the last condenser. [7] The residual gas of sulfur plan moves to remaining of gas treatment unit and the sulfur recovery increased by more processes. Otherwise, the remaining gas moves to an oxidizing and all sulfur compounds converted to SO_2 and then goes into the atmosphere. Claus process sulfur recovery efficiency is 97% and according to the concentration of the acid gas and the process used H_2S and also by increasing the catalytic reaction processes and more efficiency considerations can be reached reaction equilibrium.

Figure 3. simplified process flow diagram of a three-stage process in Pro Claus



Modeling of process furnace at Claus reaction

Mathematical modeling equations to explain the performance of the operating system means that system performance based on survival and physical laws. Regarding proposed system, as previously mentioned in this study due to lack of access to primary tool for modeling the kinetics of chemical reactions and combustion and generally lack detailed knowledge of physics, there is no possibility of implementation of all principles of logic and rational standard. Thus, using the laws of conservation of mass and energy at a microscopic level and equations to help process information, the desired output is solved and some design parameters are calculated.According to information obtained from the process of industrialization in the South Pars phases 9 and 10 can be the following assumptions as part of the preparations for the start as the accurate modeling.

(1) Due to low retention time in the furnace materials can be intrusive terms of heat and mass transfer in the axial direction compared to the terms displacement ignored.
(2) Gas combustion reaction is complete and no carbon monoxide is produced.
(3) The impact of possible adverse reactions is available regardless.
(4) Calculate the constant equilibrium of reaction in equilibrium and adiabatic flame temperature as the temperature of the combustion reaction.

Parameters that is important in Claus furnace modeling are temperature furnace and conversion of H_2S to the sulfur. [12] A purpose that is set at the specified temperature and conversion in the furnace.

Calculation of oxygen sufficient for complete combustion

The total amount of air used for combustion is 1.3 H2S. The remaining two-thirds of the reaction are to the formation of sulfur. Low and high air flow in the level of efficiency is very effective.

Acid gas inputs including H_2S , CO_2 and H_2O , and some hydrocarbons, input hydrocarbons is considered as CH_4. Combustion reaction in the furnace is as following:

$$H_2O + SO_2 \quad H_2S + 1.5O_2 \rightarrow (1)$$

$$CH_4 + 2H_2O \quad 2H_2S + SO2 \rightarrow (2)$$

Required total amount is obtained by the sum of moles O_2 obtained in the two above reactions.

3-2 calculates the equilibrium temperature of the flame using the equilibrium constant relationship

For Claus reaction in the vapor phase and at low pressure is defined as the equilibrium constant relationship in which the total pressure in the atmosphere Π : To calculate the equilibrium temperature of the reaction flame Claus will use:

$$2H_2O + \tfrac{3}{N} S_N \quad 2H_2S + SO_2 \rightarrow$$

Pi is the partial pressure of each of the combination of balance.

$$K_p = \frac{[P_{H_2O}]^2 [PS_N]^{3/N}}{[P_{SO_2}][P_{H_2S}]^2} = \frac{[MolesH_2O]^2 [MolesS_N]^{3/N}}{[MoelsH_2S]^2 [molesSO_2]} \left[\frac{\Pi}{TotalMoles}\right]^{3/N-1}$$

Due to different levels of K_p and taking a temperature, constant balance is achieved in this temperature. Then, according to the above equation and error guessing method X value is obtained.

3.3 calculate the energy obtained from reaction products

Flame temperature range is between 923 ° to 1300 ° C and we have a T in this range and calculate enthalpy products:

$$H_{tot.Reac.Product} = h_{H_2S}(\tfrac{2}{3}F_{H_2S} - X) + h_{CO_2}(F_{CO_2} + F_{CH_4}) + h_{H_20}(\tfrac{1}{3}F_{H_2S} + 2F_{CH_4} + F_{H_2O}$$
$$+ F_{H_2O(air)} + X) + h_{SO_2}(\tfrac{1}{3}F_{H_2S} - \tfrac{1}{2}X) + h_{N_2}F_{N_2} + h_{S_2}.\tfrac{3}{4}X$$

Simulation and optimization of energy consumption at sulfur recovery unit

Simulation was done using HYSYS ASPEN software in static mode. Lee- Kesler Plocker equation of state is elected.

Simulation of the reaction furnace

In process reaction furnace, conversion reactions are which strongly exothermic reaction occurs when is considered the conversion of 33% and 20% in the second reaction.

Table 1: displays flow input and output of the reaction furnace

Feature	Acid gas stream input of reaction furnace	Acid gas stream output of reaction furnace
Temperature (ºC)	220	**1400**
Pressure (kPa)	268.5	**268.5**
l/h Kgmol	328.51	**643.13**
Amount H_2S l/h Kgmol	132.23	**84.41**
Sulfur l/h Kgmol	**0**	**6.52**

Simulation of catalytic reactor

Catalytic reactors include reactor and catalyst bed.

Table 2: The results of output of reactors

Feature	Temperature (ºC)	Pressure (kPa)	MOL Kgmol/h	MOL H_2S	MOL S
Product of first reactor	313	133.5	739.12	8.56	**118.66**
Product of second reactor	226	130	615.77	4.87	**7.12**
Product of third reactor	**194**	**117**	**609.18**	**4.87**	**1.14**

Because actual information about the exit of any equipment in the flow sheet is not enough, compare for all streams are not possible.

The effect of parameters on the results of the simulation

Acid gas temperature in the furnace

Whatever acid gas inlet temperatures to sulfur is higher, the content also increases. On the other hand, the temperature of the furnace and the flame is too high as they will increase the costs of control. In addition, the amount of H_2S released in the atmosphere decreases in other words the amount of contamination in terms of emissions is reduced.

Table 3: Check the acid gas temperature in the furnace

Temperature of acid gas (Fº)	Temperature furnace (Fº)	Sulfur recovery efficiency in the whole process (%)	Sulfur recovery efficiency in furnace (%)	The amount of output of hydrogen sulfide to the atmosphere (lbmol / h)
100	597.3	51	11	**7.1**
200	613.3	66.3	20	**7**
300	1430	77.9	23	**5.6**
400	1768	96.29	48	**5.4**
500	**1827**	**97.1**	**57**	**5.4**

H_2S amount available in acid gas

It is clear that high amount H_2S available in more acidic gas, efficiency is higher. (Because of the shift in balance) On the other hand emissions of exhaust gases into the atmosphere will be increased. In simulation was performed with temperature increases with increasing H_2S acid gas was also lower inlet exhaust gases emissions. High temperatures lead to increase the production of sulfur. In other words, increasing with temperature increases H_2S acid gas inlet will tend to produce more sulfur.

Table 4: H_2S amount available in acid gas

The amount of hydrogen sulfide available in acid gas (%)	Sulfur recovery efficiency in the whole process (%)	Sulfur recovery efficiency in furnace (%)
25	91	**62.1**
35	93.1	**66.8**
45	93.7	**66.9**
55	**96.6**	**69**

Inlet air temperature

Increasing the inlet air temperature increases sulfur recovery rates. But the effect of this parameter is less acidic than the effect of the gas temperature.

Table 5: Effect of inlet air temperature

Inlet air temperature (Fº)	Sulfur recovery efficiency in the whole process (%)	Sulfur recovery efficiency in furnace (%)
100	90	**69.8**
200	91	**70.2**
300	**91.9**	**70.5**

Optimizing energy consumption in sulfur recovery unit

Due to the amount of heat generated and consumed in every part of the unit can be used in conjunction with energy conservation. The main source of heat in the unit, which is the reaction furnace temperature about C ° 1200 to C ° 1400 that source to generate low-pressure steam is another significant source of energy, burning furnace at the end of the great heat in the flue outlet will be wasted. In the meantime need to find a way through which amount of energy released by the heating process flows increased and in front of the intake flow of hot and cold utility belts. In this system for optimizing energy consumption and using a suitable heat source software package MATHLAB is provided by the software. The most important part of the sulfur recovery unit is a reaction furnace system. For this reason in order to optimize the process, optimizing the combustion section is sufficient. The results of optimization to improve the combustion and a mixture with the proper proportions, multi-valve systems or tangential injection are used to increase flow turbulence and residence time and improve process efficiency. Also installed in the furnace walls embedded raster turbulence in addition to improving in practice of mixing air and acid gas and heat balance around the furnace. If thermal cracking reactions consume can be prevented has great impact on the optimization of combustion.

Conclusions and Recommendations

Because of limitations in the lack of sufficient information about the kinetic reaction modeling, modeling was performed for macroscopic. Using the diagram at the end of the furnace and amount of conversion, the hydrogen sulfide is determined. It is obvious that if there is full information of physics and kinetics of chemical reactions and reactions optimal combustion process leads to microscopic modeling of temperature profiles, concentration and pressure in the furnace and this would help to evaluate the effect of processing on the performance of the furnace. The efficiency of sulfur recovery unit to control temperatures should always be analyzed. For each temperature change represents a

special event and most importantly the reaction furnace and the reactor. In the results of the energy optimization converters intended converters require the implementation of a new network.
One of the causes of decline in the efficiency of the unit is limited kinetic reaction furnace, so that even with respect to the amount of air necessary for the reactions due to the favorable reaction rate, in the reaction furnace output, both the oxygen and hydrocarbon unburned soot is observed. The most important factor to overcome limitations in the furnace reaction kinetics is increasing its temperature. Also, experience shows that the amount destruction of hydrocarbons largely depends on the reaction furnace temperature. Many sulfur recovery units by Claus Due to the low temperature reaction furnace problems are incomplete burning hydrocarbons, it is recommended to use various methods to increase the reaction furnace temperature some of these techniques include:
1) Fuel injection to feed
2) Pre-heat the air and acid gas to the indirect method
3) Pre-heat the air to the direct method
4) Raising the percentage of oxygen in the intake air
5) Increasing the acid gas H2S with this increase in temperature can greatly enhance amount efficiency of the unit as well as avoided the incomplete combustion of hydrocarbon in the reaction furnace.

References
1- R.N. Maddox, Gas Conditioning and Processing: Gas and Liquid Sweetening, CPS, fourth ed., (1998).
2- Andrew S. Ball, David B. Nedwell, Rupert G. Perkins, Oxidation of hydrogen sulphide in sour gas, Enzyme and Microbial Technology, 41, (2007), 702–705.
3- Ribhi El-Bishtawi, No'man Haimour, Claus recycle with double combustion process,
Fuel Processing Technology, 86, (2004), 245–260 .
4- V.F.C. Linsa, E.M. Guimara, Failure of a heat exchanger generated by an excess of SO2 and H2S in the Sulfur Recovery Unit of a petroleum refinery, Journal of Loss Prevention in the Process Industries, 20, (2007), 91–97.
5- 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, (2001), 31–43.
6- GPSA Engineering data book, tenth edition, first revision, Gas Processor supplies association Tasla, OK, (1994).
7- Sena Yasyerli, Gulsen Dogu, Timur Dogu, Selective oxidation of H2S to elemental

Gholam Hossein Gholami, MA Student in Petroleum Engineering
Mohammad Sharifi, Assistant Professor and Faculty Member of Oil and Gas University, Tehran Amir Kabir University