

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/



Parameters Control of Claus Process for Sulfur Recovery in Natural Gas Plant



Mahmoud F. Abdel Hamid^{*1}, Tarek M. Aboul-Fotouh¹, Masoud A. El-Shafie¹

¹ Mining and Petroleum Engineering Department, Faculty of Engineering, Al-Azhar University, Nasr City, Cairo, Egypt.

Abstract

Claus process is a technology to recover elemental sulfur from H₂S contained in the feedstocks, Claus Sulfur Recovery Unit is a chemical type of plant so, it is important to study the parameters that control and affect the main chemical reactions and the side reactions to obtain the maximum production of sulfur and the highest efficiency for the sulfur recovery by using the Aspen HYSYS simulation program V11. Actual data of an acid gas feedstock is obtained from a natural gas plant for this study. The feed acid gas flow rate is 0.616 MMSCFD with an H₂S concentration of 50.03 % mole introduced into the Claus Unit. This study demonstrated the optimum temperature inside the thermal reactor at 1077 °C that can be controlled and changed with the inlet temperature (the optimum 240 °C) and/or the air-to-acid gas ratio (the optimum 1.09), this temperature achieves the highest efficiency of 68.11% in the thermal reactor by taking into account H₂S-2SO₂ parameter equal 0 or little more (0.0004). The effluent gases from the thermal reactor are cooled in a waste heat boiler (WHB) to separate the produced liquid sulfur. After the WHB the remaining gases enter the first catalytic reactor where exothermic equilibrium hydrolysis reactions of COS and CS₂ and Claus reaction take place so, the chosen optimum temperature needed to be as low as possible while taking into account that the catalyst activity toward hydrolysis reactions enhanced with high temperature, the optimum temperature is 240.5 °C where COS and CS_2 conversion efficiency > 90% (the target in the first catalytic reactor) and sulfur conversion efficiency 69.37%. The produced gases from the first reactor enter the condenser to condense any sulfur vapor produced then to the second catalytic reactor, the lowest optimum working temperature is 195 °C that can apply to achieve maximum sulfur conversion efficacy of 72.91% without sulfur condensation inside the reactor and COS & CS₂ conversion efficiency 21.03% and 4.86% respectively.

Keywords: Sulfur recovery, Claus, Sour natural gas desulfurization, Claus process optimum parameters.

1. INTRODUCTION

Claus sulfur recovery process is used to get rid of H₂S produced from the sweetening process of sour natural gas to convert it to sweet natural gas [1,2]. The Claus process is a traditional chemical process for sulfur recovery where H2S is converted to elemental sulfur by burning it with air at high temperatures [3]. Claus reaction is an endothermic reaction in the thermal reactor which means the reaction rate increases with increasing the temperature inside the thermal reactor (first step) [4,5,6]. Claus reaction is an exothermic reaction in the catalytic reactor where the reaction rate increases with decreasing the temperature inside the catalytic reactors (second step) [4,5,6]. Claus process depends basically on burning one-third of H₂S feed to SO₂ and then reacting with the other two-thirds of H₂S to produce the sulfur, this takes place in two chemical reactions [<u>4,7</u>]:

 $H_2S + 1.5 O_2 \leftrightarrow SO_2 + H_2O \Delta H_r = -518 \text{ kJ moL}^{-1}$ (complete oxidation of H₂S) (1)

 $2H_2S + SO_2 \leftrightarrow 1.5 S_2 + 2H_2O \Delta H_r = +47 \text{ kJ moL}^{-1}$ (conversion reaction) (2)

and/or the dissociation chemical reaction (3) for 6% of the H₂S contained in the feed acid gas converted to sulfur; a partial oxidation reaction of the H₂S also teak place [$\underline{8,9}$]:

$$\begin{array}{l} H_2S \leftrightarrow H_2 + 0.5 \ S_2 \qquad (3) \\ H_2S + 0.5 \ O_2 \rightarrow H_2O + 0.5 \ S_2 \ (4) \end{array}$$

Up to 70% of H₂S feed is converted to elemental sulfur in the thermal reactor [4,10]. The rest of H₂S and SO₂ complete the Claus reaction at low

^{*}Corresponding author e-mail <u>mahmoudpatran111@gmail.com</u>; (M. F. Abdel Hamid). Receive Date: 28 August 2023, Revise Date: 02 October 2023, Accept Date: 22 October 2023 DOI: <u>https://doi.org/10.21608/ejchem.2023.232402.8518</u> ©2024 National Information and Documentation Center (NIDOC)

temperatures but with the presence of a catalyst in two catalytic reactors [4,7,11,12]:

 $\begin{array}{l} 2 \text{ H}_2\text{S} + \text{SO}_2 \leftrightarrow 2 \text{ H}_2\text{O} + 3/8 \text{ S}_8 \quad \Delta\text{H}_r = -108 \text{ kJ moL}^-\\ ^1 \quad (5) \end{array}$

Hydrolysis reactions take place of the side products (COS and CS₂) from the thermal reactor [8,13]:

 $\begin{array}{ll} COS + H_2O \leftrightarrow CO_2 + H_2S & (6) \\ CS_2 + 2 & H_2O \leftrightarrow CO_2 + 2 & H_2S & (7) \end{array}$

Side reactions leading to COS and CS₂ hydrolysis are important, particularly for the first catalytic reactor. If significant amounts of COS and CS₂ are formed in the thermal reactor, a higher first reactor inlet temperature is usually employed [8,13]. Approximately 90% - 95% of the COS and CS₂ formed in the furnace is decomposed in the first reactor [11, 13,14,15]. Several Claus techniques can be used in sulfur recovery plants. The straightthrough process where the total acid gas flow enters the thermal rector and controls the amount of H₂S burned by the air flow rate to burn only one-third of H₂S feed, this technology is applied when H₂S concentration is from 60-100 %. If the concentration = 50% or less it can use this technology but should preheat the acid gas feed and/or air feed to maintain the temperature inside the burner high and stable [15, 6, 16]. Split-flow process in which only one-third of the acid gas feed enters the burner and the other H₂S passes through a bypass of the burner, all H₂S that entered the burner converted to SO₂ then reacts with the remaining H₂S on the catalyst surface in the catalytic reactor, a little or no elemental sulfur formed in the burner or before the catalytic reactor so, the total sulfur recovery efficiency reduced. This

technique is applied when the H₂S concentration is from 15- 50 %. Split-flow process technique is also used when the feed contains ammonia that reacts with the sulfur compounds at low temperatures to form ammonia salts as an undesirable product so, only a third of the feed enters to burn and the reminder feed enters at the middle of the burner when the temperature high where the ammonia is thermally destroyed [8,17,18]. Direct oxidation process is applied when the H₂S concentration is lower than 15% where the air is mixed with the acid gas feed and then passed to the catalytic reactor to form SO₂ to produce the sulfur, but the catalyst is sensitive to deactivation so this technique doesn't use too much $[\underline{19}, \underline{20}]$. Acid gas enrichment technique which is used as an alternative to the direct oxidation technique at low H₂S concentrations in the feed, when in this process first increase the concentration of H₂S before the Claus burner by using an amine absorption unit [8, 21]. Oxygen enrichment process which uses pure oxygen instead of the air that contains 79% of nitrogen which needs high duty of heat and large equipment sizes, pure oxygen achieves high temperature inside the burner with low H₂S concentration and lower equipment sizes [19, 20]. The catalysts used in the catalytic reactors are alumina catalyst for Claus reaction and titaniumbased catalyst for hydrolysis reaction, two types of catalysts exit in the first reactor and only Claus catalyst in the second reactor. A tail gas treatment unit is added to increase the overall sulfur recovery efficiency by 99.5% or better (99.9+ %) but also increase the total cost required [11, 14, 21, 22, 23].

496

2. Methodology

2.1. Claus process simulation (Straightthrough process)

 Table 1 Feed condition and composition.

Feed gas flow (for 1 train)	0.616	MMSCFD
Pressure	1	barg.
Temperature	50.03	°C
i-Pentane	0.0001	Mole fractions
H ₂ S	0.5003	Mole fractions
CO ₂	0.3727	Mole fractions
H ₂ O	0.1268	Mole fractions

2.1.1. Process description and discussion

The feedstock of the acid gas is produced from the acid gas removal unit after being absorbed from sour natural gas and then injected into the Claus process to convert the H₂S chemically to elemental sulfur. The acid gas first enters the reaction furnace (thermal reactor) where the H₂S is burned based on the idea of having one-third of the H₂S contained in the acid gas feed transformed into SO₂ by controlling the air-to-acid gas flow ratio. The air and acid gas feed are preheated for thermal stabilization inside the thermal reactor (H₂S concentration is 50%) and increasing the conversion efficiency. Afterward, SO₂ is supposed to react with the remaining two-thirds of H₂S to form sulfur according to the following basic reactions:

$H_2S + 1$.	$5 O_2 \rightarrow H$	$H_2O + SO_2$	(1)		
$2H_2S + 3$	$SO_2 \leftrightarrow 1.$	$5 S_2 + 2 H_2$	2O (2)		
H_2S	\leftrightarrow	H_2	+	0.5	S_2
(dissocia	ation reac	tion) (3)			
$H_2S + 0.$	$.5 \text{ O}_2 \rightarrow \text{H}$	$H_2O + 0.5$	S_2	(1	partial
oxidatio	n) (4)				
$3 H_2S +$	$1.5 O_2 \leftrightarrow$	• 3 H ₂ O +	1.5 S ₂		(total
reaction) (8)				

The objective of this process (preheating) is to lead these reactions to near completion. When using the preheat of the air and acid gas feed is to achieve the optimum inlet temp. at the air-to-acid gas molar flow rate ratio which affects a thermal reactor Temperature, sulfur recovery efficiency, and the side reactions which lead to the formation of COS and CS₂:

 $CO_2 + H_2S \rightarrow COS + H_2O$ (9)

 $CO_2 + 2H_2S \rightarrow CS_2 + 2H_2O \quad (10)$

COS and CS_2 formation essentially depends on the concentration of CO_2 and hydrocarbons in the acid gas. The effluent gases that exit from the thermal

The acid gas flow rate, composition, pressure, and temperature used for the study using Aspen HYSYS V11 in the flowing table:

reactor are cooled in a waste heat boiler WHB (to generate steam) and then to a condenser to condense any sulfur vapor. After the sulfur is condensed the remaining gases pass to the second stage (catalytic reactors). This step is performed in two stages over an alumina catalyst; each stage of conversion is waged at optimum inlet temperature and is followed by condensation and separation of the sulfur produced in the catalytic reactor.

First Claus reactor in which alumina catalyst (10% of the catalytic bed) and hydrolysis catalyst (Titaniumbased catalyst – 90% of the catalytic bed); Claus conversion of H₂S and SO₂ to sulfur and hydrolysis reaction of COS and CS₂. The inlet temperature was determined due to an exothermic Claus and hydrolysis reaction and the catalyst activation temp. the outlet temperature increases due to the exothermic reactions. Second Claus reactor in which only alumina catalyst; Claus conversion of H₂S and SO₂ to sulfur. The low inlet temperature due to the exothermic Claus reaction and the outlet temperature increases, the reactions involved are:

$2 \text{ H}_2\text{S} + \text{SO}_2 \leftrightarrow 2 \text{ H}_2\text{O} + 3/8 \text{ S}_8$	(Claus
catalytic conversion) (5)	
$COS + H_2O \leftrightarrow CO_2 + H_2S$	(Hydrolysis
reactions) (6)	
$CS_2 + 2H_2O \leftrightarrow CO_2 + 2H_2S$	(Hydrolysis
reactions) (7)	



The following Figure (1) illustrates the Claus process simulation.

Figure (1) preheated feed and Straight Claus process.

2.1.2. Claus parameters control

2.1.2.1. Furnace (thermal reactor) Temperatur

The sulfur conversion efficiency increases with increasing the furnace temperature which increases by increasing the inlet temperature by an electric heater and/or increasing the amount of air stream/ inlet acid gas ratio; where the Claus reaction takes place with an endothermic contribution in the thermal reactor:

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

 $2H_2S + SO_2 \leftrightarrow 1.5 S_2 + 2 H_2O$ (2)

When increasing the inlet temperature and air stream/ inlet acid gas ratio it should be taken into account H₂Srecovery efficiency. So, we first start trial and error by using Aspen HYSYS with different values of the air/acid gas ratio at different inlet temperatures to get the optimum value of the air/acid gas ratio. Table 2,3,4 shows the values of air/acid gas ratios which are selected and the resulting values of outlet temp., $2SO_2 \ge 0$, COS, and CS₂ formation as low as possible in the product. The amount of air required is calculated depending on the one-third amount of H₂S in the acid gas feed:

The amount of air = 1/3 acid gas feed * $1/O_2$ concentration in air * 1.5 mole of O_2 * H_2S concentration mole fraction

= $1/3 * 1/0.2094 * 1.5 * H_2S * acid gas feed = 2.387 * 0.5003 * 0.616$

= 1.194 * 0.616 = 0.7355 MMSCFD. However, the air/acid gas ratio of 1.194 does not match with H₂S- $2SO_2 \ge 0$ and does not achieve the maximum sulfur

conversion efficiency %, H_2S-2SO_2 , and $COS + CS_2$ formation. The optimum air/acid gas ratio in each table depends on the $H_2S-2SO_2 \ge 0$, and COS and CS_2 formation.

Table 2 The air/acid gas ratio versus outlet temperatures and sulfur conversion efficiency at inlet temp. 220 °C.

Air / Acid gas ratio	Outlet Temp.	Conversion Efficiency %	H_2S-2SO_2	$\cos + \cos_2$
				Formation
0.5	762.17	22.31	0.179	0.0011
0.6	825.84	34.28	0.140	0.0014
0.7	882.90	45.64	0.105	0.0018
0.8	935.66	54.68	0.073	0.0024
0.9	984.65	60.93	0.044	0.0030
1	1028.73	65.10	0.017	0.0036
1.05	1048.97	66.55	0.0045	0.0039
1.09	1064.67	67.49	-0.005	0.0041
1.2	1105.72	69.34	-0.032	0.0047
1.3	1139.38	70.39	-0.055	0.0055
1.4	1171.27	71.02	-0.076	0.0063
1.5	1201.45	71.44	-0.096	0.0071

Table 3 the air/acid gas ratio versus outlet temperatures and sulfur conversion efficiency at inlet temp. 240 °C.

Air / Acid gas ratio	Outlet Temp.	Conversion Efficiency %	6 H ₂ S-2SO ₂	$\cos + \cos_2$
C	1			Formation
0.5	775.70	24.50	0.17	0.0012
0.6	838.70	36.90	0.13	0.0015
0.7	895.78	48.03	0.10	0.0019
0.8	948.65	56.57	0.07	0.0026
0.9	997.46	62.30	0.04	0.0033
1	1041.07	66.02	0.01	0.0039
1.09	1077.12	68.11	0.0004	0.0043
1.2	1117.11	69.78	-0.034	0.0051
1.3	1150.78	70.66	-0.057	0.0059
1.4	1182.71	71.20	-0.079	0.0067
1.5	1213.05	71.56	-0.098	0.0075
1.6	1242.86	71.79	-0.116	0.0081
1.6	1230.62	71.71	-0.114	0.0078



Figure 2 The optimum air/acid gas ratio, the outlet temp. and the conversion efficiency.



Figure 3 The optimum air/acid gas ratio, the outlet temp. and the conversion efficiency.



Figure 4 The optimum air/acid gas ratio, the outlet temp. and the conversion efficiency.

Air / Acid gas ratio	Outlet Temp.	Conversion Efficiency %	H ₂ S-2SO ₂	$COS + CS_2$ Formation
0.5	788.92	26.98	0.178	0.0012
0.6	851.61	39.52	0.139	0.0016
0.7	908.77	50.33	0.103	0.0021
0.8	961.69	58.33	0.071	0.0028
0.9	1010.21	63.53	0.042	0.0035
1	1053.28	66.83	0.014	0.0041
1.05	1073.72	67.93	0.001	0.0043
1.09	1089.15	68.69	-0.009	0.0046
1.2	1128.59	70.140	-0.036	0.0054
1.3	1162.45	70.87	-0.059	0.0063
1.4	1194.19	71.36	-0.081	0.0072
1.5	1224.80	71.67	-0.100	0.0079
1.6	1284.71	72.01	-0.134	0.0089

Table 4 The air/acid gas ratio versus outlet temperatures and sulfur conversion efficiency at inlet temp. 260 °C

Figure 2,3,4 illustrates the effect of the air/acid gas ratio on the outlet temperature and the sulfur conversion efficiency, when increasing the air/acid gas ratio the temperature increases depending on the following reaction:

 H_2S + 1.5 O_2 ↔ SO_2 + H_2O ΔH_r = -518 kJ moL⁻¹ (complete oxidation of H_2S) (1)

So, the highest efficiency will be at the highest air/acid gas ratio and also the highest temp., but reaching the optimum ratio not only depends on the thermal reactor sulfur recovery efficiency but also depends on the H₂S-2SO₂ \geq 0 which affects the total sulfur recovery efficiency of (thermal stage and catalytic stage).

Second, it will study the effect of inlet temp. on the outlet temperature and therefore the sulfur recovery efficiency to obtain the optimum inlet temp. that achieve the highest efficiency with the lowest positive $H_2S + 0.5 O_2 \rightarrow H_2O + 0.5 S_2$ (4)

which increases the sulfur conversion efficiency (at high temp.) that follows the reaction:

 $2H_2S + SO_2 \leftrightarrow 1.5 S_2 + 2H_2O \Delta H_r = +47 kJ moL^{-1}$ (conversion reaction) (2)

So, the chosen air/acid gas ratios in each table are selected at the positive value of H_2S-2SO_2 before the first negative value.

The study shows that the optimum air/acid gas ratio 1.09 observed in Table 3 where are the highest efficiency 68.11 with the lowest positive value of H₂S- $2SO_2 = 0.0004$.

value of H₂S-2SO₂ at the air/acid gas ratio of 1.09 from the previous study. Table 5 shows different values of inlet temperatures with the resulting outlet temp. and sulfur recovery efficiency values.



Figure (5) The effect of furnace temperature on sulfur recovery efficiency.

Inlet temperatures (acid gas feed and air	Outlet temperatures	Sulfur conversion efficiency %
feed)		
30	951	56.88
65	972.8	59.7
85	985.5	61.02
105	998	62.34
125	1010	63.53
145	1023	64.61
165	1035	65.57
185	1047	66.43
205	1059	67.18
225	1072	67.83
240	1077	68.11
245	1084	68.44
265	1096	68.94
285	1108	69.41
305	1119	69.87
325	1131	70.22
345	1142	70.5
565	1274	72
665	1345	72.19
765	1425	72.28
865	1510	72.31

 Table 5 The inlet temperatures versus outlet temperatures and sulfur conversion efficiency

Figure (5) shows that the sulfur conversion

efficiency becomes almost constant from 1274 °C, the chosen working temperature depends on the maximum efficiency from the thermal reactor, H₂S-2SO₂ parameter ($H_2S-2SO_2 = 0$ to protect the TGT section where the excess of SO₂ plugs TGT and Quench column) and the side product formation (COS and CS₂ which increase with increasing the temperature). It is suggested a little excess of H₂S for H₂S-2SO₂ \ge 0 and COS and CS₂ formation is as low as possible, but more excess of H₂S reduces the produced sulfur. So, the chosen temperature is 1077 °C with inlet temp. 240 °C to achieve 68.11% sulfur recovery efficiency in the thermal reactor and H₂S-2SO₂ in the flue gas to TGTU = 0.0048 - 2* 0.0022 = 0.0004 with air stream/ inlet Acid gas ratio = 1.09. Figure (5) explains the effect of furnace temperature on sulfur recovery efficiency.

2.1.2.2. The inlet temperature of the first catalytic reactor

Hydrolysis reactions of COS and CS₂ and Claus reactions are exothermic equilibrium reactions enhanced by low temperature in the catalytic reactors, but the COS and CS₂ to H₂S conversion efficiency rate of COS and CS₂ to H₂S but in the same time decrease the Claus reaction rate that improves with low temperature so, the chosen working temperature 240.5 °C where COS and CS₂ conversion efficiency almost become constant > 90 % (the main target in the first catalytic reactor) and sulfur conversion efficiency 69.36%. Figure (6) explains the effect of 1st catalytic reactor inlet temperature on the hydrolysis reactions of COS, CS₂, and the sulfur conversion efficiency.

increase with increasing temperature because the

temperature enhances the catalyst activity toward

hydrolysis reactions hence improving the conversion

2.1.2.3. The inlet temperature of the second catalytic reactor

The inlet sulfur dewpoint temperature at this condition is 175 °C, so it is necessary to put a margin (safety factor +20 °C) to avoid the sulfur condensation inside the catalyst that causes catalyst deactivation. The chosen working temperature is 195 °C is the lowest temperature to achieve maximum sulfur recovery efficiency which increases with decreasing the temperature. The sulfur recovery efficiency is 72.91% and COS and CS₂ conversion efficiency is 21.03% and 4.86% respectively. Figure (7) illustrates the effect of 2nd catalytic reactor inlet temperature on the

hydrolysis reactions of COS, CS_2 , and the sulfur conversion efficiency.



Figure (6) The effect of 1st catalytic reactor inlet temp. on the hydrolysis reactions and the sulfur conversion efficiency.



Figure (7) The effect of 2nd catalytic reactor temperature on the hydrolysis reactions and the sulfur conversion efficiency.

2.1.3. Results

Table 6 The optimum values of the most important control parameters in the Claus process at H₂S 50.03 mole%

The tail gas flow rate	1.15	MMSCFD
Pressure	0.6497	barg.
Temperature	150	°C
Hydrogen	0.0139	Mole fractions
Argon	0.0054	Mole fractions
Nitrogen	0.4558	Mole fractions
СО	0.0097	Mole fractions
CO ₂	0.1903	Mole fractions
H ₂ S	0.0048	Mole fractions
COS	0.0001	Mole fractions
SO ₂	0.0022	Mole fractions
H ₂ O	0.3174	Mole fractions
S ₆ _Vapor	0.0001	Mole fractions
S ₈ _Vapor	0.0003	Mole fractions

Table 7 The condition and composition of the tail gas produced from the Claus section to the TGTU			
The optimum air/acid gas molar flow ratio in the thermal reactor °C	1.09		
The optimum inlet temp. of the thermal reactor °C	240		
The optimum outlet temp. of the thermal reactor °C	1077		
The optimum inlet temp. of the first catalytic reactor °C	240.5		
The optimum inlet temp. of the second catalytic reactor °C	195		
The amount of H ₂ S-2SO ₂ factor	0.0004		
The sulfur recovery efficiency of the thermal reactor %	68.11		
The highest total sulfur recovery efficiency of the thermal stage + the catalytic stage $\%$	96.214		

2.2. **TGT process simulation**

2.2.1. Process description and discussion

The main purpose of this process is to convert all the sulfur components contained in the tail gas from the Claus section to H₂S that is recycled back to the absorption section, and therefore increase the total sulfur recovery efficiency; the feed streams are tail gas from the Claus train, sweep gas from the sulfur drum, fuel gas, and combustion air; the effluents are tail gas to the multipurpose absorber in the absorption section and process water. First, the feed is preheated and the reducing gases are generated in the generation stage in the in-line heater where the reducing gases (H₂ and CO by sub-stochiometric burning of fuel gas) are necessary for the conversion reactions in the catalytic stage, and preheat the tail gas from the Claus trains and the sweep gas from the degassing section by mixing with the flue gases from the in-line heater. Partial oxidation of the fuel gas (methane) reaction:

 $CH_4 + 0.5 O_2 \rightarrow CO + 2H_2$ (heat) (11)

The mixture gases from the in-line heater enter the hydrogenation catalytic stage where the hydrogenation catalyst (cobalt molybdenum oxide) (COMOX) reduces all sulfur compounds contained in the tail gas from the Claus section into H₂S over a catalytic reactor by the following reactions:

Hydrogenation reactions:

 $SO_2 + 3H_2 \leftrightarrow H_2S + 2H_2O$ (12) $S_x + xH_2 \leftrightarrow xH_2S$ (13) Hydrolysis reactions:

 $CO + H_2O \leftrightarrow H_2 + CO_2$ (Water Gas Shift) (14) $COS + H_2O \leftrightarrow H_2S + CO_2$ (Hydrolysis) (6)

$CS_2 + 2H_2O \leftrightarrow 2H_2S + CO_2$ (Hydrolysis) (7)

Then the flue gases from the catalytic stage are injected into the cooling stage to cool the tail gas before recycling it to the absorber since lower temperatures favor the absorption process.

The following figure (8) illustrates the simulation of the hydrogen generation and hydrogenation conversion stage.

2.2.2. TGT parameters control

2.2.2.1. H₂ Parameter

In all the TGT reactions H₂ is involved, after the quench cooling tower, the excess of hydrogen produced in the Inline Heater monitors the complete SO₂ conversion in H₂S inside the reactor (H₂ vol % > 0.03%).

2.2.2.2. Air/Fuel gas ratio

Most of the H₂ is produced in the inline heater where the fuel gas (CH₄) is burned under a sub-stoichiometric (the selected sub-stoichiometric combustion ratio 80 %) combustion by the following reactions:

 $CH_4 + 0.5 O_2 \leftrightarrow CO + 2H_2$ (11)

 $CO + H_2O \leftrightarrow H_2 + CO_2$ (Water Gas Shift) (14)

(Sub-Stoichiometric combustion) 75%-90% Stoichiometric Air – between 7.1 - 9.0 ratio.

If the air-to-fuel gas ratio decreased below 7.1 (using Aspen HYSYS where some CH4 is still unburned in the tail gas from the inline heater) he carbon component will be produced then it poisons the hydrogenation reactor catalyst.

 $CH_4 + O_2 \leftrightarrow C + 2H_2O$ (Soot Formation) (15) <75% Stoichiometric Air / <7.1 ratio.



Figure (8) The simulation of the hydrogen generation and hydrogenation conversion stage.

2.2.2.3. Hydrogenation reactor temperature

To have good efficiency in SO₂ conversion the temperatures inside the reactor have to be maintained between 180 $^{\circ}$ C and 400 $^{\circ}$ C depending on the type of

the catalyst, these reactions in the hydrogenation reactor are exothermic and therefore are favored by lower temperatures. The temperature regulation is limited by the fact that the catalyst used is active only at a specific temperature which is considered the minimum operating temperature [23, 24].

 Table 8 The condition and composition of the tail gas produced from the TGT section to the absorption section

The tail gas from the quench column flow rate	1.181	MMSCFD
Pressure	0.4018	barg.
Temperature	33	°C
Hydrogen	0.0344	Mole fractions
Argon	0.0072	Mole fractions
Nitrogen	0.6021	Mole fractions
СО	0.0005	Mole fractions
CO ₂	0.2209	Mole fractions
H ₂ S	0.0099	Mole fractions
COS	0.0000	Mole fractions
CS ₂	0.0000	Mole fractions
SO ₂	0.0000	Mole fractions
H ₂ O	0.1250	Mole fractions
S ₆ _Vapor	0.0000	Mole fractions
S ₈ _Vapor	0.0000	Mole fractions

3. Conclusion

The Claus process is a chemical process used to convert the H₂S produced from the sour natural gas to elemental sulfur, this process is subject to several parameters which affect the sulfur recovery efficiency. The conversion of H₂S to sulfur is accomplished through the thermal section and catalytic section, in the thermal reactor the parameter that affects the sulfur conversion efficiency is the thermal reactor temperature which is affected by the air/acid gas ratio and inlet temperature. So, the air/acid gas ratio was studied first at different inlet temperatures to get the optimum air/acid gas ratio (1.09) at which the maximum sulfur recovery efficiency (68.11%) taking into account the $H_2S-2SO_2 \ge 0$ (0.0004), then studying the effect of the inlet temperature on the conversion efficiency to get the optimum inlet temperature (240 °C) at which the maximum sulfur recovery efficiency. In the catalytic reactor, the parameters that affect the sulfur conversion efficiency are the inlet temperatures of the first catalytic and second catalytic reactors where the sulfur conversion efficiency in the two reactors increases with decreasing the inlet temperature but the temperature was limited by the catalyst activity toward hydrolysis reactions (in the first reactor) which was enhanced with high temperature (240.5 °C), and the sulfur dewpoint temperature of 175 °C (in the second reactor) to avoid the sulfur condensation inside the catalyst that causes catalyst deactivation, so the second reactor inlet temperature conducted with safety factor (+20 °C) to be 195 °C . In all the TGT reactions H₂ is involved so the H₂ generation is important for hydrogenation and hydrolysis reactions. The hydrogen is generated under Sub-stoichiometric combustion from 75%-90% of the fuel gas (CH₄) (Air/Fuel gas ratio between 7.1 - 9.0), when the air-to-fuel gas ratio decreases below 7.1 the carbon component will be produced that poisons the hydrogenation reactor catalyst.

References

[1] Polasek JC, Bullin JA. Effect of sulfur recovery requirements on optimization of integrated sweetening, sulfur recovery, and tail gas cleanup units. The USA: Bryan Research & Engineering Inc., 1993:170-4.

[2] Nagamalleswararao Kanidarapu, Juma Haydary, Studies on Sulfur Recovery Plant Performance Using Aspen HYSYS Sulsim Simulations, Petroleum and Coal, January 2019.

[3] El-Bishtawi R., Haimour N, Claus Recycle with Double Combustion Process, Fuel Process. 2004 Technol. 86, 245.

[4] Mohamed Sassi and, Ashwani K. Gupta, Sulfur Recovery from Acid Gas Using the Claus Process and High Temperature Air Combustion (HiTAC) Technology, American Journal of Environmental Sciences, May 2008.

[5] Samane Zarei, Hamid Ganji, Maryam Sadi, Mehdi Rashidzadeh, Kinetic modeling and optimization of Claus reaction furnace, Journal of Natural Gas Science Engineering, and April 2016, doi.org/10.1016/j.jngse.2016.03.086.

[6] Nader Javanmardi Nabikandi, Shohreh Fatemi, Kinetic modeling of a commercial sulfur recovery unit based on Claus straight through process: Comparison with equilibrium model, Industrial and Engineering Chemistry, May 2015,

doi.org/10.1016/j.jiec.2015.05.001.

[7] R. Abedini, M. Koolivand Salooki, S. Ghasemian, Modeling And Simulation Of Condensed Sulfur In Catalytic Beds Of Claus Process: Rapid Estimation, Chemical Engineering Research, November 2010, DOI:10.3329/cerb.v14i2.5595.

[8] H. Ghahraloud, M. Farsi, M.R. Rahimpour, Modeling and optimization of an industrial Claus process: Thermal and catalytic section, Journal of the Taiwan Institute of Chemical Engineers, July 2017. doi.org/10.1016/j.jtice.2017.03.005.

[9] Suna An, Ji Chul Jung, Kinetic modeling of thermal reactor in Claus process using CHEMKIN-PRO software, Case Studies in Thermal Engineering, October 2020, doi.org/10.1016/j.csite.2020.100694.

[10] Farhad Fazlollahi, Sajjad Asadizadeh, Milad Ahmadi Khoshooei, Mohammad, Reza Sardashti Birjandi, Majid Sarkari, Investigating Efficiency Improvement In Sulfur Recovery Unit Using Process Simulation And Numerical Modeling, Oil & Gas Science and Technology - - Rev. IFP Energies Nouvelles 76, 18, 26 Feb 2021.

[11] Najah Abumounshar, Abhijeet Raj, Salisu Ibrahim, Novel Processes For Lean Acid Gas Utilization For Sulfur Production With High Efficiency, Chemical Engineering Science 248 117194, 14 October 2021.

[12] Abhijeet Raj, Salisu Ibrahim, Anoop Jagannath, Combustion Kinetics Of H2S And Other Sulfurous Species With Relevance To Industrial Processes, 14 April 2020

[13] Bahman ZareNezhad, An investigation on the most important influencing parameters regarding the selection of the proper catalysts for Claus SRU converters, Industrial and Engineering Chemistry, August 2008, doi:10.1016/j.jiec, 2008.08.020.

[14] Salisu Ibrahim, Ramees K. Rahman, Abhijeet Raj, Dual-Stage Acid Gas Combustion To Increase Sulfur Recovery And Decrease The Number Of Catalytic Units In Sulfur Recovery Units, Applied Thermal Engineering 156 (576–586), 25 April 2019 [15] Xun Tao, Xinlei Yu, Songling Guo, Fan Zhou, Yunfei Gao, Lu Ding, Zhenghua Dai, Fuchen Wang, Oxy-fuel combustion of lean acid gas for high sulfur recovery efficiency based on straight-through Claus process, January 2023, doi.org/10.1016/j.jgsce.2022.204868.

[16] W. D. Monnery, K. A. Hawboldt, A. Pollock, W. Y. Svrcek, New experimental data and kinetic rate

[19] Anne Piéplu, Odette Saur, Jean-Claude Lavalley, Oliver Legendre, Christophe Nédez, Claus Catalysis and H2S Selective Oxidation, Science and Engineering, March 2013, doi.org/10.1080/01614949808007113.

[20] G McIntyre, L Lyddon, Claus Sulphur Recovery Options, Petroleum Technology Quarterl, Bryan Research and Engineering, Inc. – 1997, Technical Papers.

[21] Hamid Reza Mahdipoor, The Influence of Acid Gas Loading On The Performance Of Acid Gas Enrichment (Age) Absorber Column, International Journal of Chemical and Petroleum Sciences, 2015.

[22] Yasser Al Wahedi, Ana I. Torres, Saleh Al Hashimi, Norman I. Dowling, Prodromos Daoutidis,

expression for the Claus reaction, Chemical Engineering Science, 2000.

[17] Salisu Ibrahim, Ramees K. Rahman, Abhijeet Raj, A split-flow sulfur recovery process for the destruction of aromatic hydrocarbon contaminants in acid gas, January 2022, doi.org/10.1016/j.jngse.2021.104378

[18] Flavio Manenti, Davide Papasidero, Eliseo Ranzi, Revised Kinetic Scheme for Thermal Furnace of Sulfur Recovery Units, AIDIC Conference Series, 2013, 11, 221-230 DOI: 10.3303/ACOS1311023.

Michael Tsapatsis, Economic Assessment Of Temperature Swing Adsorption Systems As Claus Tail Gas Clean Up Units, 16 December 2014.

[23] Araby I. Mahdy, Abeer M. Shoaib, Mohamed M. Gamal4, Khaled I. Behery, Walaa S. Osman, Optimization of Sulfur Recovery and Tail Gas Treatment Units Using Aspen Hysys and Matlab Integration, Egypt. J. Chem. Vol. 66, No. 5 pp. 303 – 314, September 2022.

[24] Kuo-Tseng Li, Yao-Chun Hung, Hydrogenation of sulfur dioxide to hydrogen sulfide over Fe/ γ Al2O3 catalysts, Applied Catalysis B: Environmental 40, 2003, doi.org/10.1016/S0926-3373(02)00009-7. M. F. Abdel Hamid et.al.